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Preamble

AGH University of Science and Technology is the technical university that deals with scientific topics important for Poland, which fit in with the latest global trends.

Energy sector is exercising changes and challenges that never occurred in the past. The transformation of the fuel and energy sector, and its impact on the environment and human health, is a basic problem in the modern world. The direction of changes in this industry may lead to economic growth and an improvement in the quality of life of citizens but also raises concerns about reliability, energy supply prices and social security in the era of new technology development. Contemporary problems of fuel and energy economy and related environmental problems should be classified as interdisciplinary issues, possibly to be solved mainly on the international forum. New scientific issues, technological challenges and problems of the economy of fuel and energy processes are analysed in terms of their impact on climate change, human health and the safety of the natural environment

Introduction of support systems for renewable energy sources has led to the increase of their share in power generation. On one hand, it helps to mitigate the air quality problem, but, on the other hand, as RES have still high capital costs and low capacity factor in Polish conditions, they contribute to increasing the energy costs for final costumers. Additionally, their intermittent nature requires completely new working conditions of the electricity supply system, mainly, more flexible operation of classical fossil generators to cover the residual load. Their unpredictability requires also maintaining the back-up capacity, ready to balance the disappearing supplies. Development of high capacity storage technologies could help to overcome the balancing problems. High hopes are also placed on the development of the hydrogen economy, expected to play a major role in the energy transition.

The Conference EFE 2022 is organized biennially by the Faculty of Energy and Fuels of AGH University together with the Institute of Thermal Power Engineering of Cracow University of Technology. We hope that the Conference will contribute to deeper understanding of the discussed processes, as well as allow to find the means to solve both large and small problems of the fuels and energy sectors.

Monika Motak
Magdalena Dudek
Bogdan Samojeden

Silica Supported Visible Light Active Graphitic Carbon Nitride (G-C3n4) Photocatalyst for Estrogenic Hormones Removal And Antibacterial Activity

Hassan Ali[1]*, Milan Masar[1], Muhammad Yasir[1], Fahanwi Asabuwa Ngwabebhoh[1], Oyunchimeg Zandraa[1], Tomas Sopik[1], Michal Machovsky[1], Ivo Kuritka

Keywords: g-C3N4, photocatalysis, estrogens, hormones, antibacterial activity

ABSTRACT

In this study, we report on a silica-supported graphitic carbon nitride photocatalyst synthesized via a facile heat treatment route of urea and characterized by XRD, SEM, FTIR, and UV-vis spectroscopy. The photocatalytic activity of the as-prepared sample was evaluated by the photodegradation rate of four major estrogenic hormones (E1, E2, EE2, E3) under visible light LED irradiation at λ_{max} ~ 425 nm. The degradation results showed that the as-prepared sample possessed considerable adsorption affinity for all the tested hormones as well as robust photocatalytic efficiency. Owing to the synergistic adsorptive and photocatalytic activity, elimination rates of 82, 93, 83, and 96% were achieved for the E3, E2, EE2, and E1 hormones, respectively. In addition, antibacterial tests showed that the as-prepared sample possessed reasonable antibacterial activity against the gram-positive (*Staphylococcus aureus*) and gram-negative (*Escherichia coli)* bacteria.

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Simulation and Determination of Crude Oil Fouling in Laboratory Tests

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Keywords: fouling, crude oil, fouling simulation, fouling deposits

ABSTRACT

Fouling is generally defined as the deposition and accumulation of unwanted materials such as solid or semi-solid substances on the heat transfer surfaces. In the refining industry fouling deposits are formed due to physical and chemical processes, that occur when crude oil comes into contact with the high temperature of the metal surface in the heat exchangers. Fouling can occur throughout the refinery and can affect heat exchanger trains in almost every refinery unit. The unique chemical composition of crude oil or blends of crude oils, the type and amount of asphaltenes present, and the compatibility of crude oil composition may determine its fouling potential. Refineries currently face a great challenge of accepting harder to process blends of crude oils from different sources, resulting in risk of fouling and products instability. Fouling deposits reduce heat transfer and equipment thermal efficiency, causing a major financial losses in oil refineries. Estimations of the extra energy requirements caused by fouling deposition range from no less than 10% to over 30%. This is not only the energy cost problem, but it is also an environmental issue due to increased release of greenhouse gas emissions. Costs associated with heat exchanger fouling include also: increased capital investment, additional operating costs (cleaning exchangers) and production losses. For this reason, it is extremely important for the refining industry to prevent crude oils incompatibility, and to determinate crude oil fouling on a laboratory scale prior its processing.

Oil and Gas Institute use for fouling simulation of refinery streams unique simulator - The Falex Thermal Fouling Tester and Refinery Process Analyzer (RPA). This simulator is helpful for research projects and production studies of heat exchanger fouling tendencies. A fluid sample is passed over a pressurized tube-in-shell heat exchanger for a set duration of time. Fouling is shown by a decrease in outlet sample temperature and physical deposit on the heater exchanger. After the test exchanger used is weighted and the formed deposits are examined directly on its surface. The simulator was used for determining fouling of selected crude oil samples, previously tested for basic physico-chemical properties including: distillation range, asphaltene content and colloidal instability factor. Chemical characterization of obtained fouling deposits was carried out using: optical microscopy, scanning electron microscopy (SEM-EDX) and FTIR-microscopy. For each of tested crude oil, a different type of deposit was obtained on the model heat exchanger - in the form of: corrosion products, inorganic salts and coke-like material. The determination of crude oil fouling carried out with the use of Falex simulator, will allow to optimize the composition of crude oil blends in order to reduce fouling deposits on an industrial scale.

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History and State of the Art of Hydrogen and its Use in Gas Turbines

Krzysztof Badyda[1,*]

Keywords: hydrogen and ammonia as CO_2 free energy carriers, hydrogen gas turbine, power generation, low NO_x hydrogen combustion technologies

ABSTRACT

Presentation will include review of most important issues related to the history and future use of hydrogen for energy purposes. The background will be comment regarding impact of the current economic situation on the possibilities of hydrogen generation and use in power sector. Exemplary, as can be read two years ago in [1] "*Estimated costs today for fossil-based hydrogen are around 1.5 €/kg for the EU, highly dependent on natural gas prices, and disregarding the cost of CO_2 . Estimated costs today for fossil-based hydrogen with carbon capture and storage are around 2 €/kg, and renewable hydrogen 2.5-5.5 €/kg. Carbon prices in the range of EUR 55-90 per tonne of CO_2 would be needed to make fossil-based hydrogen with carbon capture competitive with fossil-based hydrogen today*". Today, the prices of fossil fuels are many times higher, the cost of hydrogen generation from them has increased dramatically. Price of CO_2 is near to 90 EUR per tonne. An illustration of this new price level influence, based on natural gas costs is provided in Figure 1. As cost components are included: purchase of natural gas and CO_2 emission only.

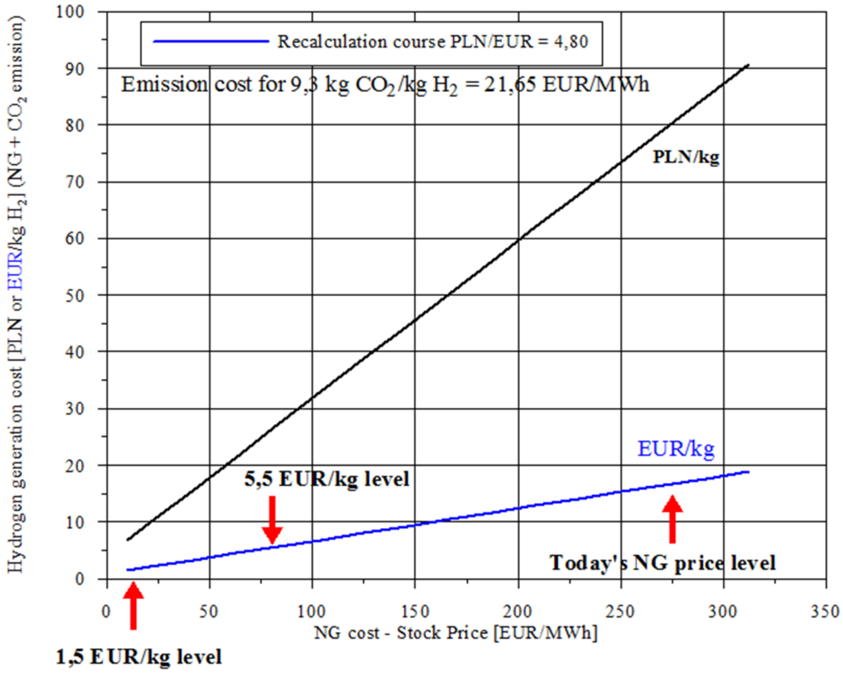

Figure 1. „Gray" hydrogen generation and associated CO_2 emission cost. Estimated CO_2 emission of 9.3 kg to produce 1 kg of (gray) hydrogen – methane reforming.

Besides that information related different fuels used in the gas turbines now and in the future, including these do not generating CO_2 emissions, will be presented. Properties of hydrogen and ammonia as a fuels and significant differences in relation to the natural

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gas, strategies for low-emission generation and use of hydrogen, including power generation will be commented.

Next presented issues concern prospective scale of utilities demand, including water for electrolysis and electricity from renewables, state of the art of hydrogen co-firing and firing technologies developed by heavy duty gas turbine deliverers.

[1] A hydrogen strategy for a climate-neutral Europe, Brussels, COM(2020) 301 final.

Case Studies on Waste Heat Recovery and Cogeneration via Thermoelectric Generators

Ali Cemal Benim[1,*]

Keywords: TEG, Heat and fluid flow, waste heat recovery, cogeneration

ABSTRACT

A thermoelectric generator (TEG) is a semiconductor device, which achieves a direct conversion of heat in to electrical energy [1]. The electric power produced by a TEG is strongly influenced by the applied heat sink. While a TEG is aimed at harvesting waste heat, the optimization of the efficiency of the heat sink is a key task for the design of waste heat recovery systems implementing TEG. A TEG model is proposed and implemented in an open source toolbox for field operation and manipulation (OpenFOAM) for the purpose of performing optimizations of the heat sink, using a commercially available TEG as basis. This model includes the multi-physics thermoelectric coupled effects. Conservation principles of energy and current are considered simultaneously. This includes the thermal and electric conduction, Seebeck effect, Peltier effect, Thomson effect, and Joule heating. Much attention is paid to model validation. On the one hand, different modelling aspects are validated based on the measurements from the literature. On the other hand, specialized experiments are performed on an in-house test rig, which is developed to this purpose. Within this framework, aspects are explored, which have not been investigated in detail before, including the effect of variable temperature patterns.

Based on the models, TEG applications are presented, which aim the utilization of waste heat from a forging process and cogeneration from the abundantly available heat released by biomass combustion. Optimization procedures are additionally utilized in designing the corresponding cooling systems.

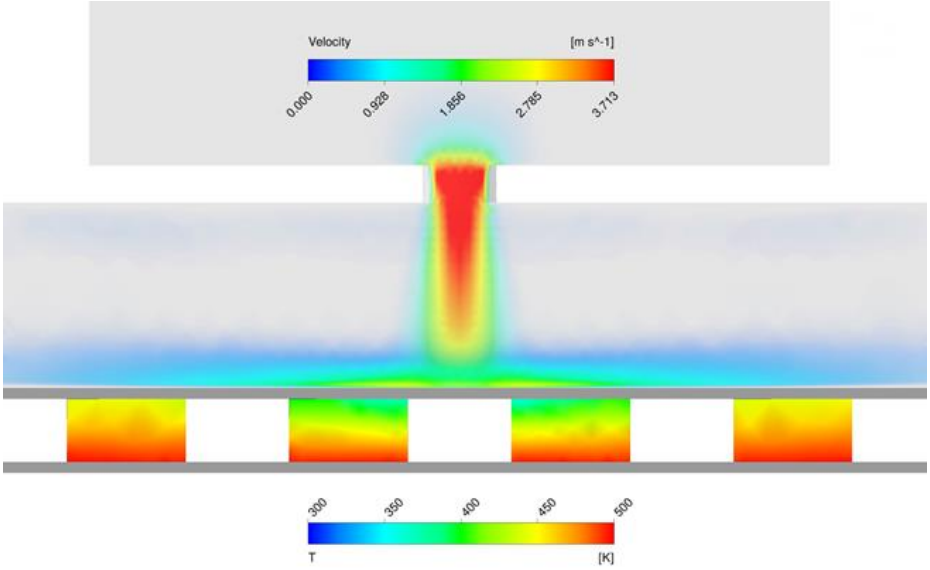

Figure 1. Velocity and temperature distributions for impingement cooling of a TEG array

[1] S. W. Angrist, Direct Energy Conversion, 3rd edition, University Press, Cambridge.

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Environmental aspects of the use of biomass to produce high-energy materials

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Keywords: Biomass, high-energy materials, waste disposal

ABSTRACT

Explosives for civil uses are commonly employed in mining for rock excavation and engineering purposes (demolition works, demining). They provide the cheapest method of obtaining rock and energetic materials in opencast mining. About 45,6 million kg (2021) of explosives are used for mining purposes in Poland each year. Rock material is obtained with the use of explosives. Commonly used explosives include emulsion explosives (EE) and ammonium nitrate/fuel oil explosives (ANFO), which are the second most popular explosives for civil uses in opencast mining, as presented in Fig. 1.

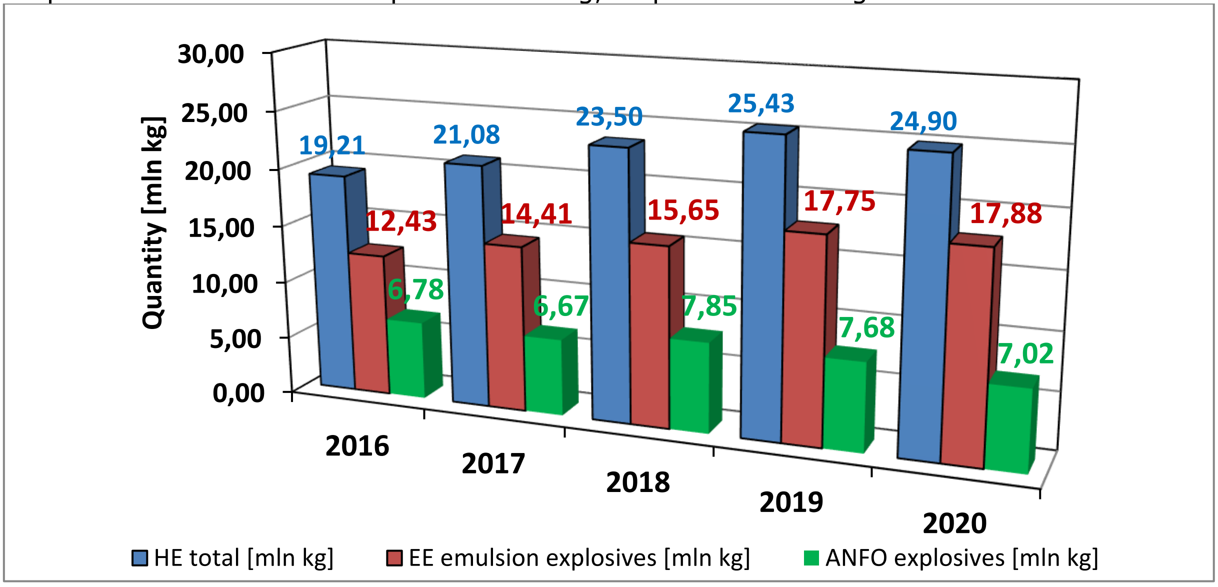

Fig. 1. Explosives used in opencast mines in 2016-2020 [1,2]

Due to the development of urban planning and the increase in the global population, huge amounts of waste are generated and consumption contributes to the production of biomass waste, which is a key social and environmental concern. World production of plant biomass waste (generated as a result of agricultural and forestry activities) amounts to 140 Gt per year. Proper management of such waste may contribute to minimizing the harmful impact on the environment in the case of landfilling (an element of waste management). The guidelines for proper waste management are the waste hierarchy recommended by the European Waste Framework Directive (2008/98/EC and 2018/851).

Agricultural biomass is primarily used for the production of biofuels. It is estimated that by 2050, energy from biomass will cover more than 50% of energy needs in most developed countries. Poland plans to generate at least 80% of total energy from renewable sources, including biomass. More than 75% of biomass energy is to be produced from agricultural biomass [3].

Undertaking research on the use of biomass is important due to the wide array of

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possible applications of this waste raw material as a source of energy in explosives. To date, biomass has mainly been used as a renewable energy source.

One of the essential parameters in assessing the promise of the discussed materials (waste materials) is their calorific value. Calorific value is defined as the amount of heat released during the combustion of fuel with a specific mass or volume, assuming complete and total combustion. Table 1 presents the thermo-physical properties of selected biomass types compared to that of hard coal.

Tab. 1 Selected thermo-physical properties of biomass from agricultural production [4]

Fuel	**Calorific value [MJ/kg]**	**Heat of combustion [MJ/kg]**	**Ash content [%]**	**Volatiles [%]**	**Moisture content [%]**
Straw	14.66	15.94	3.31	64.97	11.20
Hay	16.39	17.58	4.57	70.85	5.80
Sunflower shells	17.68	18.94	1.57	66.60	7.90
Walnut shells	18.88	20.13	1.12	72.28	6.80
Sunflower grain	28.07	29.32	3.32	81.69	7.70
Pumpkin seeds	25.27	26.48	4.29	80.19	5.60
Corn grain	14.71	16.05	1.06	73.27	13.20

An unconventional and innovative way of using biomass is its use for the production of high-energy (explosive) material. The basic components of explosive mixtures are an oxidizing agent and fuel. To modify explosive compositions, biomass, depending on its type and origin, can be added replacing individual components in such a way as to obtain an oxygen balance (BT) of the mixture close to the optimal (zero).

The most promising substance will be the one that modifies the explosive while ensuring that all of its explosive properties are as close to those of the original substance as possible (the values characterizing the reference explosives currently available from manufacturers), or even better. This would allow a reduction in the production costs of explosives while providing similar or improved performance characteristics. The use of energy properties of biomass for the purposes of explosive production may contribute to environmental benefits consisting of the reuse of waste, which is part of the broadly understood idea of recycling and the circular economy.

Industrial scale production of ANFO from biomass can reuse large amounts of waste substances. In Poland, for the purposes of blasting works only in opencast mines, about 7 million kg of EX are used annually (according to data from 2020). Assuming the production of only 20% of ANFO, out of this value containing 1.0% of biomass in its composition, it is possible to reuse 14,000 kg of the waste substance per year [3].

The study methodology will be based on developing new compositions for explosives containing biomass, estimating the performance characteristics, conducting studies of properties of the obtained explosives regarding their production and application safety and performance characteristics.

The study will provide the chemical composition of a new explosive (or new explosives) that fulfill the project objectives, as well as the technology for its manufacture, including industry producibility.

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[2] The state of safety in the performance of blasting works in opencast mining, Brochure of the Higher Mining Authority 2021.
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Agricultural fertilizers produced from sewage sludge - aspect of the presence of pharmaceuticals

Wioleta Bolesta[1,2] , Marcin Głodniok[3], Barbara Kasprzyk-Hordern[4], Katarzyna Styszko[1]

Keywords: pharmaceuticals, sewage sludge, fertilizer, wastewater treatment plant

ABSTRACT

The problem of the increasing production of sewage sludge in the wastewater treatment process forces to use economic and ecological methods of their management. One of the most commonly practiced is the agricultural use of sewage sludge.

Particular attention was paid to the processing of stabilized sewage sludge into granular organic-mineral fertilizer. Such a fertilizer is a complete product that can be used in agriculture. It is rich in nitrogen and phosphorus necessary for the development of plant organisms.

Like sewage sludge, fertilizer is subjected to restrictive analyzes in the context of the presence of parasites and the content of heavy metals. In addition, the fertilizer, after it has been approved and issued by the relevant authorities, can be approved for marketing.

It should be remembered that along with the sewage sludge, "micro-pollutants" are also disseminated, which include pharmaceuticals derived from human and animal metabolism, and not decomposed during the wastewater treatment process.

The use of sewage sludge and the resulting fertilizer in agriculture will inevitably contribute to the spread of poorly known 'new emerging contaminants'.

The aim of this study is to analyse the content of bactericidal drugs in sewage sludge and organic-mineral fertilizer, formed on the basis of the sludge, and to identify the possibility of leaching these substances into the water phase of the soil.

The study covered sewage sludge stabilized by mesophilic methane fermentation and the resulting granular fertilizer and the liquid formed after the soil pharmaceutical substances leaching test.

For this purpose, solid samples (sewage sludge and fertilizer) were frozen and freeze-dried. After weighing out the grinded small aliquot of the sample (0.5 g) and sieving the particles with particle size not greater than 0.45 µm, an internal assay pharmaceutical standard (50 ng) was added. The sample was then extracted with ultrasound and the addition of acetonitrile.

The extracted compounds were subjected to liquid chromatography (LC) analysis coupled with mass spectrometry (MS). Liquid chromatography mass spectrometry (LC-MS/MS) was performed using a Waters, ACQUITY UPLC ™ (Ultra-Performance Liquid Chromatography) system coupled to a Xevo TQD-ESI mass spectrometer and a BEH C18 reverse phase column (Waters, Manchester, Great Britain). The conditions have been optimized for fast chromatographic separation and high sensitivity across different drug classes. The best organic separation and purification was achieved with the mobile phase A composed of H_2O: MeOH with 0.1% formic acid in the ratio 95:5 and the mobile phase B consisting of 100% MeOH.

The leaching test consisted in subjecting the fertilizer to shaking with deionized water for a specified period of time in accordance with PN-EN 13266 *Slow-release fertilizers. Determination of the release of nutrients. Method for coated fertilizers*. The obtained over-

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sediment water was subjected to SPE and UPLC extraction under identical conditions for the analysis of solid samples.

For sixteen compounds analyzed, the concentrations of four were below the limit of quantification. It has been reported that the concentration of sulfasalazine and ketoconazole is up to ten times higher than that of other pharmaceuticals. Eight compounds showed a reduction after treatment of stabilized sewage sludge, in contrast to penicillin V and ofloxacin. The concentration of these two substances was higher in the fertilizer than in the sludge from which it was formed. These compounds were clearly concentrated. In other words, ofloxacin and penicillin V are not photocatalyzed or oxidized. These processes, however, underwent sulfasalazine, sulfapyridine, pyrazinoic acid 5-hydroxy-, delamanid, pyrazinamide, erythromycin, emtricitabine which is observed in the reduced amount of these drugs in the fertilizer.

The fate of a pharmaceutical in the production of a fertilizer depends on the individual properties of the substance.

Table 1. The fate of a pharmaceutical during the production of fertilizer

1	Sulfonamides	**Sulfamethoxazole**	<LOQ
2		**Sulfasalazine**	reduction
3		**Sulfapyridine**	reduction
4		**Sulfadiazine**	<LOQ
5	Chemotherapeutic agents	**Trimethoprim**	<LOQ
6		**Metronidazole**	<LOQ
7	Beta Lactam Antibiotics	**Penicillin V**	increase in concentration
8	Fluoroquinolones	**Ofloxacin/Levofloxacin**	increase in concentration
9		**Pyrazinoic acid 5-Hydroxy-**	reduction
10	Antifungal drugs	**Ketoconazole**	reduction
11	Anti-tuberculosis drugs	**Delamanid**	reduction
12		**Pyrazinamide**	reduction
13		**Isoniazid**	no change
14	Macrolide	**Erythromycin**	reduction
15	Antiviral drugs	**Emtricitabine**	reduction
16	Oxazolidine antibiotics	**Linezolid**	no change

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Use of adsorption chillers integrated with solar collectors for air conditioning systems

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Keywords: solar adsorption chiller, solar cooling, sustainable development

ABSTRACT

Currently, there is a dynamic increase in the demand for cooling, which directly translates into a constantly increasing number of refrigeration units [1,2]. Among others, this is influenced by global warming, which manifests itself through increasing average temperatures on Earth and more and more frequent temperature extremes. Moreover, the progressive urbanization and economic development additionally contribute to such an intensive development of the refrigeration and air conditioning sector. When analysing the refrigeration market, it is important to note that it is dominated by compressor refrigeration systems, which are powered by electricity. These devices are characterized by high efficiency and relatively low price, which are their main advantages. Nevertheless, special attention should be paid to the high electricity consumption of compressor chillers. A report by the International Institute of Refrigeration in Paris indicates that the refrigeration sector consumes around 20% of global electricity [2]. In 2019 air conditioning units accounted for approximately 8.5% of electricity consumption worldwide, generating 1 GT of CO_2 emissions [3]. These facts clearly make it necessary to pay attention to alternative cooling technologies which include, among others, sorption refrigeration systems. Sorption chillers can be supplied with heat at a temperature above 70 °C. Then they are absorption systems. Whereas chillers powered by low-temperature heat with temperature in the range of 50-90 °C are adsorption units. Adsorption chillers are a promising alternative to conventional refrigeration technologies. Their widespread use may result in a global reduction in electricity consumption and a reduction in greenhouse gas emissions. Thus, adsorption chillers may become an important tool in the current energy transformation and constitute a response to the crisis on the raw materials market.

The possibility of supplying adsorption systems with low-temperature heat, besides the utilisation of waste heat, also enables the use of renewable energy sources for this purpose. One of these is solar energy. The possibility of integrating adsorption chillers with solar thermal collectors has already been investigated many times, but it has been limited to considering these systems in hot climate zones with regions such as Southern Europe, the Middle East or African countries. In this study, the authors analysed the possibility of using solar collectors to power an adsorption chiller in the climatic conditions prevailing in Poland. The main aim of the research was to determine the coefficient of performance (COP) and the cooling capacity of the device operating in the analysed climate zone. In addition, the obtained results make it possible to determine the validity of the use of this type of hybrid installation in climatic conditions that are characteristic for Poland. The obtained results are the next step in planning the transformation of the energy sector in Poland, with particular focus on the cooling industry, the growing role of renewable energy sources and the need to implement a circular economy.

The system that is the subject of this study (Fig. 1) is located at the PAS Research Centre Energy Conversion and Renewable Resources in Jablonna, Poland. The system consists of four basic components: an adsorption chiller (SorTech, eCoo 2.0), a solar collector unit (Kingspan Thermomax DF400 and HP 400), borehole thermal energy storage (BTES) and buffer tanks.

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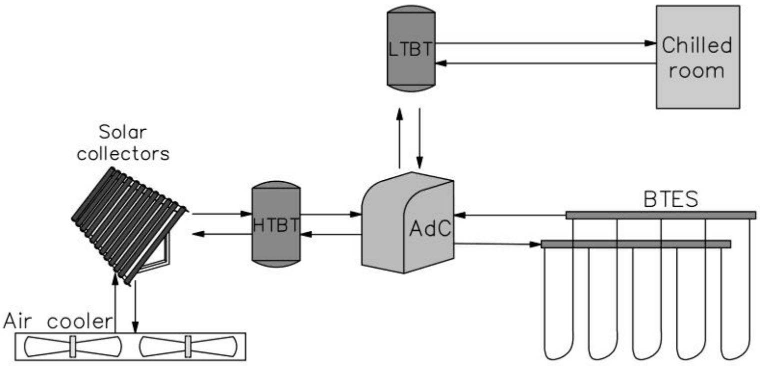

Figure 1. Diagram of the system: (AdC) adsorption chiller; (LTBT) low temperature buffer tank; (HTBT) high temperature buffer tank; (BTES) borehole thermal energy storage

Using this measuring system, measurements were made between 9 a.m. and 15 p.m. during the summer months of June, July and August. The values measured during the experiment allowed to determine the cooling power and heating power for each measuring point. Final comparative analyses were performed for 6 selected days. Hot water and chilled water flows were analysed. Moreover, the inlet and outlet temperature of the heating water and chilled water circuits were also analysed. Table 1 presents a summary of the main operating parameters of the chiller, which were obtained by integrating the relevant curves in the graphs (it is due to the fact that the sampling time during the measurements was 1 s).

Table 1. Summary of the basic operating parameters of the system for the analysed days

Date [DD.MM]	Average solar radiation [W/m^2]	Average cooling capacity [kW]	Average heating power [kW]	Average COP [-]	Average hot water temperature [°C]	Average chilled water flow [kg/s]	Average chilled water temperature [°C]
08.07	424.1	7.18	13.36	0.605	61.7	0.474	11.7
22.07	718.9	8.71	13.32	0.677	57.7	0.471	12.5
31.07	647.0	5.16	14.27	0.400	60.2	0.471	8.6
06.08	642.8	6.79	13.54	0.584	62.0	0.473	8.1
11.08	621.4	7.83	15.19	0.584	67.6	0.475	12.7
21.08	627.2	7.53	14.00	0.582	62.5	0.478	11.1

Based on the research and analysis of the results, it was found that the adsorption coolers available on the market can be successfully used in the climatic conditions characteristic of the Polish region. Nevertheless, when designing this type of systems, particular attention should be paid to longer stabilization time in relation to compressor units and appropriate selection of thermal energy and cold storage capacities, so as to ensure stable operation of the adsorption chiller.

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Content of ecotoxic elements in the main fractions of municipal solid waste

Marcelina Bury[1], **Tadeusz Dziok**[1,*]

Keywords: waste, alternative fuels, thermal treatment, ecotoxic elements,

ABSTRACT

Currently, the management of municipal solid waste (MSW) for energy production is of increasing importance. According to regulations, this type of waste can only be combusted in facilities meeting the relevant requirements. The combustion temperature and residence time in the combustion chamber are important. Waste incineration plants must also monitor and control emissions of heavy metals [1]. These are: As, Cd, Cu, Co, Cr, Hg, Mn, Ni, Pb, Sb, Tl, and V. Additionally, emissions of sulfur and chlorine compounds must be controlled. These elements are classified as ecotoxic, which has a negative impact on human health and the environment [2].

MSW is characterized by significant variability in the content of ecotoxic elements. This is due to both the varying content of the particular fractions and their different origins. The study aimed to determine the content of ecotoxic elements in the main fractions of MSW. Samples of paper waste, cardboard, textile, plastics, plastic film, glass, and rubber were collected. Additionally, samples of RDF fuel produced from MSW, as well as sewage sludge from municipal wastewater plants, which is commonly used as an addition to RDF, were analyzed.

The samples were homogenized and ground. The different properties of the samples required the use of an appropriate grinding method: (i) the LMN-100 knife mill from Testchem (paper waste, cardboard, textiles, and plastic film); (ii) the Freezer/Mill 6870D cryogenic mill from SpexSamplePrep (plastics, rubber, and RDF); (iii) the LAB-09-200 cylindrical-ring mill from EKO-LAB (sewage sludge caked after the drying process). All the samples were ground to less than 0.5 mm. The determination of ecotoxic elements was performed according to the relevant standards for waste.

The content of ecotoxic elements in the samples analyzed is shown in Table 1. Among the samples analyzed, the highest content of particular ecotoxic elements was recorded for rubber (S), plastics (Cl), and RDF (heavy metals). The waste types for which the lowest content of ecotoxic elements was obtained included paper waste, (the lowest reported content of heavy metals), textiles, and glass. It should be noted that very high variability was recorded regardless of the ecotoxic element analyzed. The coefficient of variation ranged from 113% to 178% for sulfur and mercury, respectively. Therefore, the combustion of MSW which is a mixture of different types of waste poses a serious hazard to the environment and human health.

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Table 1. Content of ecotoxic elements in analyzed waste samples

Group of sample	Type of sample	$S_{t.d}$, %	Cl_d, %	Hg_d, µg/kg	$(Cd+Tl)_d$[2], mg/kg	$(Sb+As+Pb+Cr+Co+Cu+Mn+Ni+V)_d$, mg/kg
MSW fraction	Paper waste	0.10	0.25	7	<0.06[1]	63
	Cardboard	0.11	0.14	19	0,12	82
	Textiles	0.25	0.19	17	<0.06[1]	94
	Plastics	0.27	3.83	5	0.19	67
	Plastic film	0.28	0.81	5	0.77	68
	Glass	<0.02[1]	0.01	<1[1]	<0.06[1]	457
	Rubber	1.73	0.13	64	0.65	153
Alternative fuel produced from MSW	RDF-1	0.33	1.43	1 476	3.99	601
	RDF-2	0.66	1.81	787	1.39	1717
	RDF-3	0.26	0.67	47	0.50	391
Others	Sewage sludge	1.28	0.22	517	1.33	654
Statistical parameters	average	0.48	0.86	268	0.83	395
	min	0.02	0.01	1	0.06	63
	max	1.73	3.83	1 476	3.99	1717
	range	1.71	3.82	1 475	3.93	1654
	CV[3]	113%	133%	178%	140%	125%

[1] below the limit of quantification; [2] presented as Cd. For all samples, thallium content was recorded below the limit of quantification (<1.0 mg/kg); [3] the coefficient of variation.

Acknowledgments

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Challenge of hydrogen and carbon dioxide in the energetic paradigm: case of devices based on molten carbonates

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Keywords: Hydrogen, carbon dioxide, molten carbonates, fuel cell, electrolyser

ABSTRACT

Hydrogen is an "energy vector" becoming a major issue in the present energetic bouquet. Enormous programs are appearing all over the world related to the use of such a "fuel", potentially present in the organic world, in water and even as a natural gas. The problematic of this small molecule is complex, because it must be first produced, then stored and utilized directly or in an electrochemical system called "fuel cell". In this first part, a panorama of the present energy situation, including all the classical energies, and showing the role of hydrogen in a future economy based on renewable energies. The relevant topic of clean production of hydrogen (green hydrogen) by electrolysis in different fuel cells devices at low and high temperature will be described, indicating some research routes.

CO_2 emissions are nowadays above 40 Gt per year; it is therefore compulsory to decrease them significantly in view of global warming control. The key challenge is the storage and/or the conversion of this molecule. The unique properties of molten carbonates make them among the most efficient solvents to solubilize CO_2 and, furthermore, reduce it into valuable fuels CO, CH_4, C. In this second part, a focus is given on high temperature applications of such electrolyte. The Molten carbonate Fuel Cell (MCFC), a mature technology, can be used as a reference device for absorbing and exploiting CO_2 molecule. Precisely, determining the solubility of CO_2 in molten carbonate eutectics is crucial to the development of carbon capture & electrolysis systems and the mechanistic understanding of CO_2 behavior in such media. Recent results will be given on co-electrolysis of H_2O and CO_2 in molten carbonates combining theoretical, speciation, simulation & electrolysis data.

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Moving away from Russian gas: A holistic lifecycle comparison between Russian gas and American LNG

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Keywords: LCA, NG, LNG, Energy Security

ABSTRACT

The Russian war in Ukraine has led to a fragmented geopolitical landscape, questioning historically stable energy economic relations between the Kremlin and Brussels. Therefore, the whole of Europe is socially and politically rethinking energy security, the European Union (EU) as well as the International Energy Agency are calling for a more diverse strategy for energy supply in Europe [1].

Russian natural gas imports account for approximately 45% of European gas imports [2]. Focusing on Germany, the share increases up to 55% and 55.6 bcm [3]. A shift from Russia as a natural gas supplier is therefore a highly complex task that cannot be solved by a single measure. LNG imports to the EU can, however, substitute a significant share of Russian gas imports. By early 2023, Germany expects to implement two Floating Storage and Regasification Units (FRSUs) with a total capacity of 14 bcm per year. This will be upscaled further to four FSRUs by 2024, with a fifth unit already being discussed [4]. As US LNG shows the most promising prospects in terms of deployment and political commitment, this alternative has been chosen for a holistic comparison to natural gas imports from Russia to Germany.

To assess the environmental impact, a lifecycle assessment with a cradle-to-gate approach is performed for both alternatives from natural gas production until the injection into the German natural gas grid. First results suggest an environmental advantage of Russian gas over US LNG with a carbon footprint difference of ca. 15%. Furthermore, the US LNG supply chain seems to be more sensitive to production leakages – an important aspect, given that recent studies revealed significant underestimations of production leakage rates in the US [5]. On a national scale, Germany's emissions are calculated to increase up to 50 MtCO2e if all Russian gas were to be substituted by LNG. Finally, the adverse nature of fracking and its impact on the supply chain would be revealed in its high impact on freshwater and marine ecotoxicity. When validating the results, operator's recent annual reports stated emission levels which were 30-50% lower compared to the ecoinvent LCA database entries [6]. This suggests that improvements along the supply chains have been effective in reducing greenhouse gas emissions over the last years.

Nevertheless, the current gas crisis can not only be assessed from an environmental perspective; economic and social aspects must be considered. From an economic perspective, long-term natural gas contracts with Russia lead to a more stable price corridor. In contrast, LNG import prices are more variable and have therefore a wider spread impact on Germany's GDP. Additionally, energy poverty and other social indicators must be assessed to gain insights into the effects on society. In addition, the fact that Russian gas revenues can be partly used for military actions against Ukraine is a social aspect that must also be carefully considered. Even though the need for the switch in supply is not debatable, the change needs to be evaluated from a more holistic perspective. Including environmental and social aspects besides the economic impact is necessary for policymakers and regulators to obtain energy security for the EU.

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Thermovolumetric examinations of steam gasification of tire char supported by catalyst based on biomass ashes

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Keywords: waste management, steam gasification, tire char, biomass ashes as catalyst

ABSTRACT

This work aimed to assess the feasibility of steam gasification of industrial tire char and the impact of supporting the process with various types and amounts of biomass ashes as catalysts. Sunflower husk ash – SHA, beet pulp ash – BPA, beech chips ash – BCA and corn cobs ash – CCA (characterised by a high but varied content of alkali and alkaline earth metals, especially K and Ca) in an amount of 5, 10 and 15 wt.%, were selected as catalysts for the process [1]. Samples of tire char and char-catalysts were subjected to gasification in isothermal conditions (in the range of 800-1000 °C or 800-900°C, respectively) under the pressure of 1 MPa, using the thermovolumetric method based on an analysis of the composition of the resulting gas. Based on the measurements, the changes in the formation rates of main gas components (CO, H_2, CO_2 and CH_4) were determined. Moreover, the maximum carbon conversion, times of partial (50%) conversion, yields of the gas components, percentage gas composition and H_2/CO ratio were designated. Moreover, kinetic parameters (activation energy Ea and pre-exponential factor A) of carbon conversion reaction were calculated using the grain model (GM) and random pore model (RPM). The non-catalytic gasification measurements proved that at 1000 ℃, the process was efficient, whereas at lower temperatures (especially 800 ℃), it requires support by catalysts. Catalyst addition and increasing its loading up to 15 wt.% improved the reactivity of the tire char at temperatures up to 850 ℃. Moreover, the catalysts had a significant but temperature-dependent impact on gas components yields. However, the selected catalysts favoured both carbon-steam reaction and water gas shift reaction; and the highest CO yields were obtain for SHA, and the highest H_2 yields for BCA (with the highest Ca content). Kinetics parameters were reduced due to catalysts addition, whereas the lowest values were generally obtained for 5 wt.% of catalysts (especially SHA). Thus, catalytic tire char gasification performed under appropriately selected conditions (temperatures of 800-850 °C, presence of 10/15 wt.% of catalysts, especially SHA/BCA) may be an attractive way to obtain a valuable hydrogen-rich gas efficiently.

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Impact of the rotational disintegrator speed on the effectiveness of the sewage sludge disintegration process

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Keywords: hydrodynamic disintegration, energy density, organic compounds release, non-Newtonian fluid, Herschley-Bulkley model

ABSTRACT

The aim of the study was to determine the rotational speed impact on the performance of rotational disintegrator. The analyzed substrate was sewage sludge from Warsaw sewage treatment plant. The research covered mathematical modelling and bench tests. The mathematical model of the processes occurring in the device was built and implemented in Ansys CFX numerical environment. The rotor was modelled as immersed solid. The medium was treated as non-Newtonian fluid described with Herschel-Bulkley equation. The model viscosity parameters like consistency index, power-law index or critical shear rate, were determined experimentally. Calculations were conducted in the transient mode and covered three pre-selected rotational speeds, for each of them three states were analyzed: initial, intermediate and final. The example velocity profile in the cross section of the device with the pressure contour on the rotor walls is shown in the Fig.1. Results analysis allowed to assess the cavitation zones. The low pressure volume (equal or below cavitation pressure of water in 20°C) for the example case is presented in the Fig. 2.

The determination of hydrodynamic disintegration (HD) efficiency before and after the process involved control of dissolved SCOD values. The disintegration process was conducted in a range of energy density (EL) 35-210 kJ/L with a step every 35 kJ/L for the following three engine revolution speeds (R): 1500, 2500, and 3000 rev/min. Temperature and viscosity of sediments was also controlled. The tests covered thickened excess sludge originated from a biological municipal wastewater treatment plant.

Fig. 3 presents changes in the SCOD value depending on the energy density used in the disintegration process and with consideration of the engine revolution speed. They reveal that together with an increase in the R value, the sewage sludge released a higher amount of organic compounds, whereas the intensity of the process increased with an increase in EL (Fig. 4).

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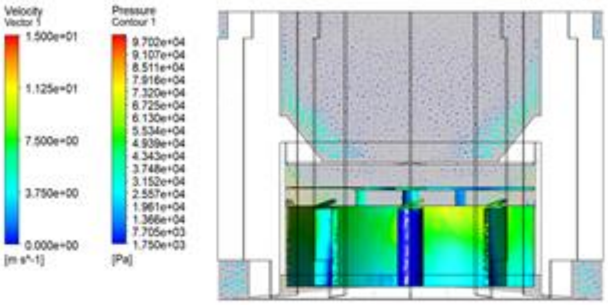

Figure 1. Velocity vectors and pressure contour on the rotor walls, rotational speed 1500 rev/min, energy density 35 kJ/L.

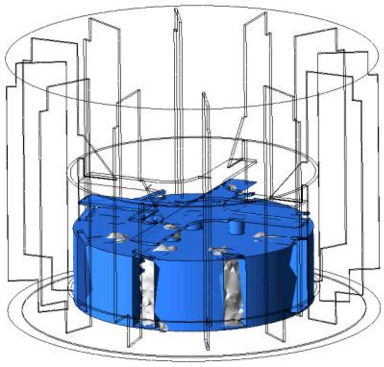

Figure 2. Zones of the pressure below the cavitation pressure of water (1705 Pa), rotational speed 3000 rev/min, energy density 35 kJ/L.

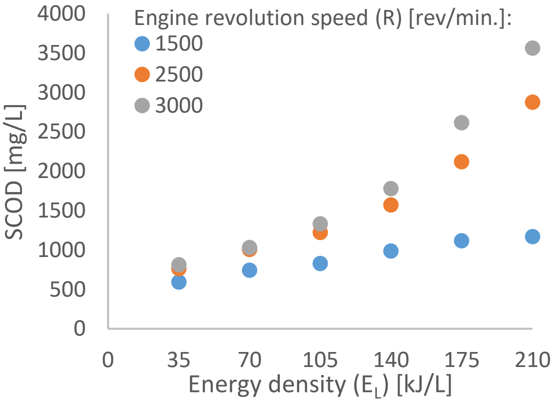

Figure 3. SCOD values obtained in an example experiment.

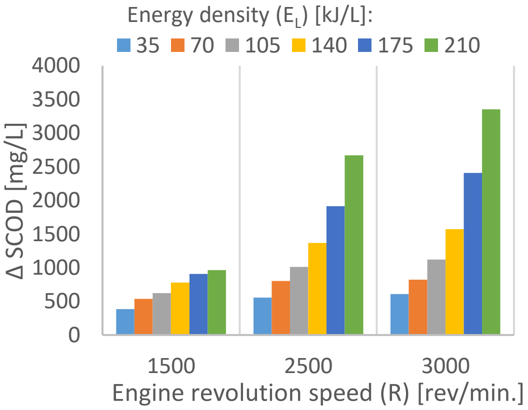

Figure 4. Amount of released organic compounds org (ΔSCOD) depending on the engine revolution speed for different energy densities used in the disintegration process.

The energy and economic analysis of flue gas heat recovery systems improving the energy efficiency of gas cogeneration units

Piotr Dzierwa[1,*], Jan Taler[2], Patryk Peret[1], Marcin Trojan[1], Dawid Taler[1]

Keywords: heat recovery systems, cogeneration unit, energy efficiency

ABSTRACT

One of the most efficient ways of combined heat and power production is gas-fired cogeneration units consisting of gas engines coupled to generators. At present, standard solutions allow the recovery of heat from the cooling process of the engine casing and the cooling of the exhaust gas up to approximately 100-120°C. The installation of an additional flue gas heat recovery stage would make it possible to increase the efficiency of CHP units by reducing the so-called chimney loss.

This study concerns an energy and economic analysis of flue gas heat recovery systems for the most commonly built cogeneration units at Polish CHP plants with a total thermal and electrical capacity of approx. 9 MW and a fuel input of approx. 10 MW. For the calculations, an example of the temperature distribution of the return water from the district heating network during the year was assumed.

First, the benefits of adding an additional economiser to pre-heat district heating water were analysed (Figure 1 (A)). Next, a heat recovery system was simulated to cool the flue gases to lower temperatures (also below the dew point temperature) using an absorption and compressor heat pump (Figure 1 (B)). The heat from the flue gases would then be absorbed by the cooling water in the circuit between the heat exchanger on the flue gases and the bottom source of the heat pump.

On the basis of the determined amounts of additional heat recovery and the assumed investment and operating costs of the extended CHP units, the economic viability of the proposed solutions was estimated and compared.

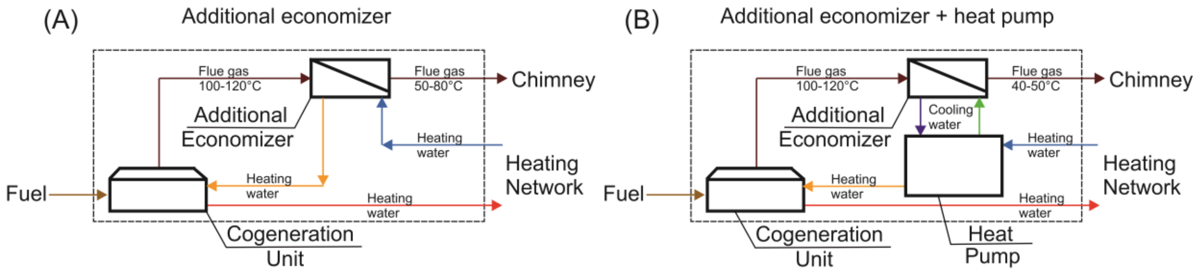

Figure 1. Schematic diagram of flue gas heat recovery system

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A system for the recovery, storage and use of waste heat from the minted molding sand

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Keywords: waste heat recovery from the minted molding sand, energy saving, CFD modeling, thermal energy storage

ABSTRACT

The subject of the paper is research on developing a complete system for the recovery, storage and use of thermal energy from minted molding sand. Heat removal from the molding sand is important because of the proper control of the MF unit process and the possibility of using the heat from its cooling.

Molding sand is a mixture of molding ingredients selected in the right proportions and in the right way, providing optimal strength and technological properties in the foundry industry.

The slow cooling of the minted sand makes it impossible to use it quickly in the regeneration station and return it to the foundry process. The recovered heat can be used for other energy-intensive processes in the foundry. Currently, the methods of recovering this heat and its further use are unknown.

A concept for a heat recovery system has been developed. The proposed system allows the use of the heat contained in the molding mass minted from large molds with temperatures in the range of 350 to 400 ^{o}C. The permissible mass temperature at the inlet to the regeneration station should not exceed 90 ^{o}C; the most favorable temperature limit is 60 ^{o}C.

In a single day, about 200 tons of molding sand are recovered from broken molds. In the plant, the work is done in a two-shift mode, hence there are 100 tons of molding sand to be cooled per shift. Considering the eight-hour operation, 12.5 tons of molding sand must be cooled in one hour. The original plan was to build a system to recover heat from the minted molding sand based on a vibrating channel or screw cooler. However, the initial work already showed that this would not be a feasible solution. The calculations showed that it would be necessary to use large-scale systems, which is impossible due to limited space.

Water with a variable inlet temperature will be used to cool the molding sand. It is assumed that the molding mass will be cooled in a vertical cylindrical tank, where finned pipes will be placed. The exchanger dimensions are based on the amount of space available for construction. It is planned to build two exchangers with an inner diameter of the shell equal to 3 m and a height of up to 6 m. It is estimated that both tanks will be filled with about 120 tons of molding compound. The above information defines the cooling capacity of the molding sand.

Computer simulations of the exchanger's operation were carried out first. Several variants of the number and arrangement of finned tubes inside the heat exchanger were modeled, which made it possible to select the optimal design of the heat exchanger. The results of CFD simulations in ANSYS-CFX software for the selected cooling system are shown in Figure 1.

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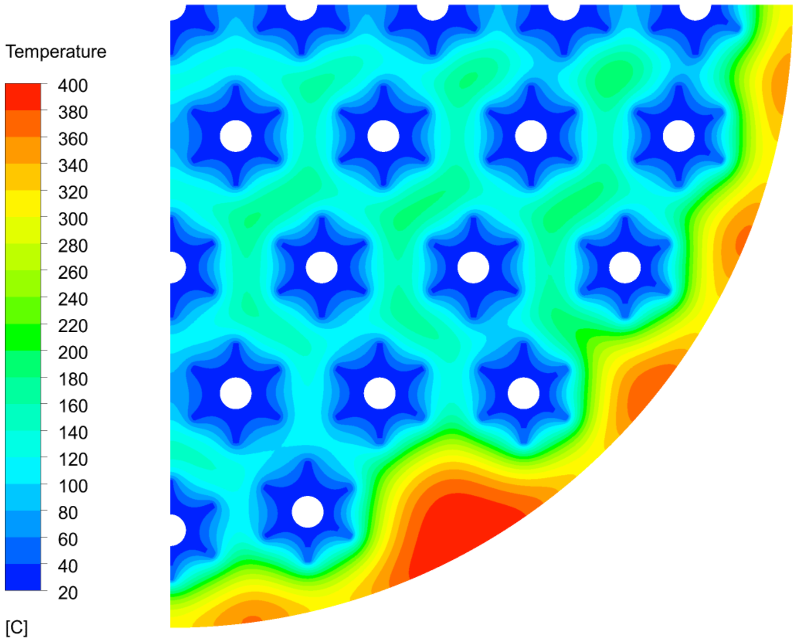

Figure 1. Temperature distribution in the cross-section of the heat exchanger at 180 minutes of cooling the molding sand.

The results show that the molding sand can be cooled quickly while providing a capacity of 12 t/h.

For the proposed finned-pipe heat exchanger design, additional thermal-strength analyses were carried out using the finite element method. It was assumed that the upper part of the finned tube is welded to the body of the exchanger, while the lower part is free to expand. The heat load was read from an unsteady heat transfer analysis. Figure 2 shows the temperature distribution in the finned tube after 6 hours of cooling.

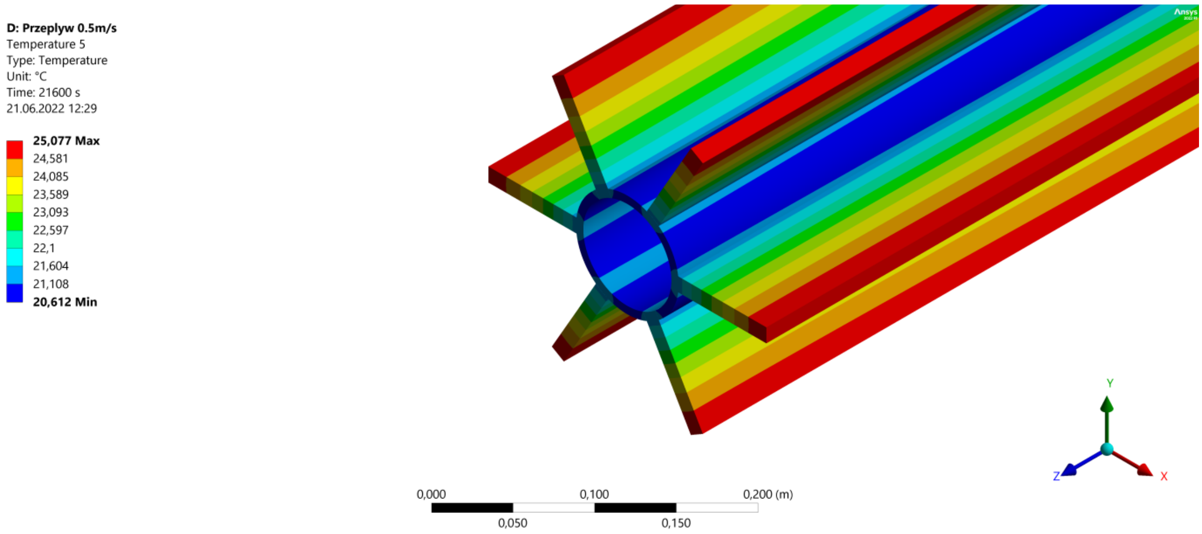

Figure 2. Temperature distribution in the finned tube after 6 hours of cooling.

Figure 3 shows the distributions of reduced stresses calculated according to the Huber-Mises-Hencky hypothesis and normal longitudinal stresses (in line with the pipe axis) after 6 hours of cooling.

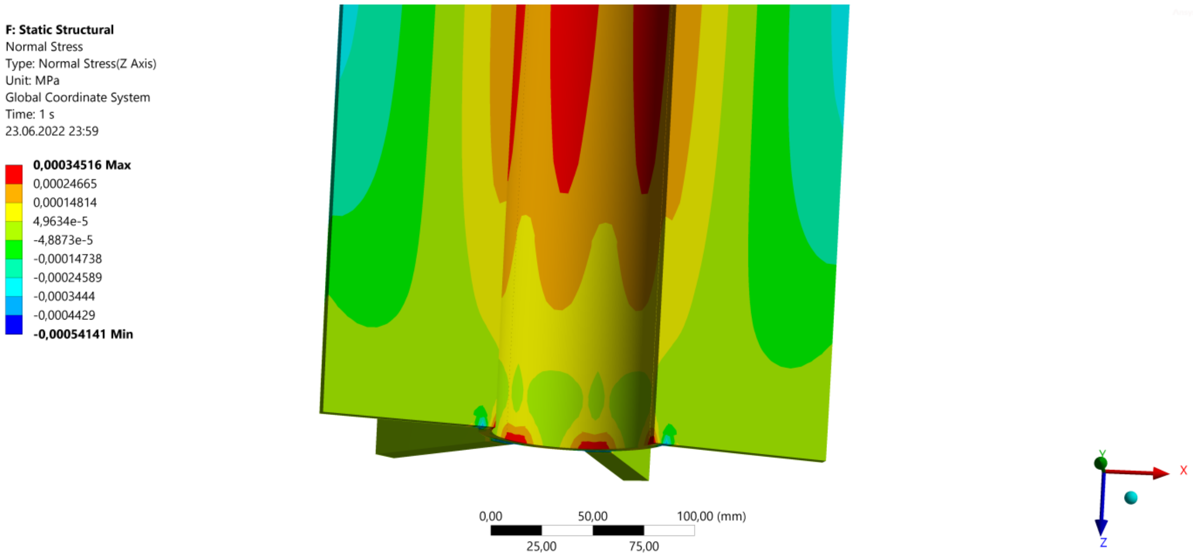

Figure 3. Distribution of circumferential stress after 6 hours of cooling.

Based on the calculations, it can be concluded that the highest stresses prevail at the beginning of the cooling process when the most significant temperature differences occur. With time, the temperature gradients decrease, decreasing thermal stresses to essentially negligible values.

Measurements were carried out on the designed test stand to verify the assumptions and the developed mathematical models. Figure 4 shows a photo of the complete test stand, which was made and built at Krakodlew Foundry.

Figure 4. Finished test stand.

A numerical model of the test stand was made. The simulation results obtained were compared with the test results. Figure 5 shows the temperature distribution of the molding sand in the stand after 60 minutes of cooling, determined by numerical modeling.

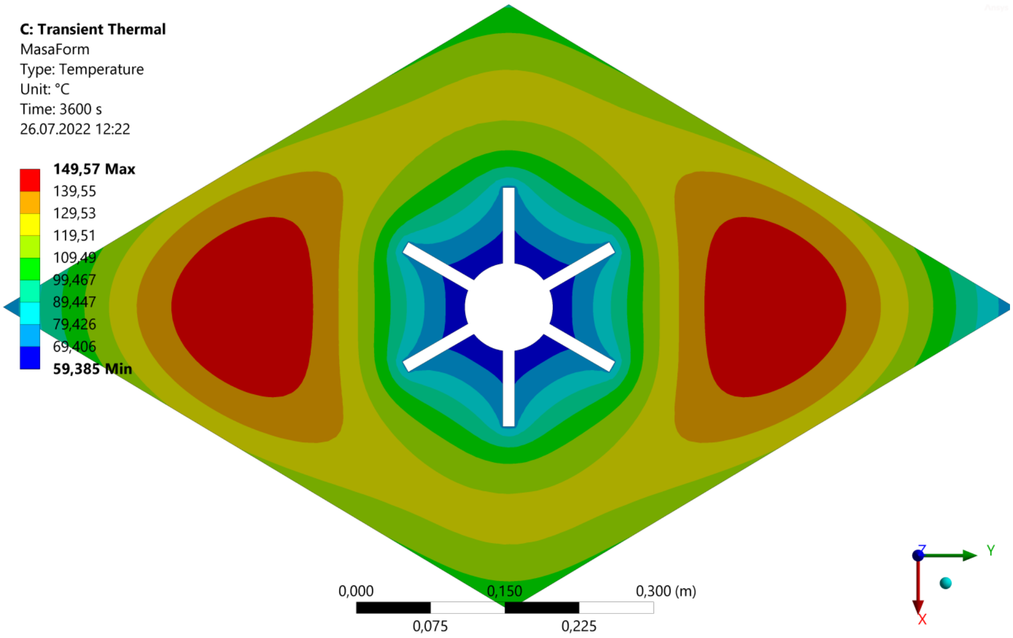

Figure 5. Temperature distribution of the molding sand in the stand after 60 minutes of cooling.

Simulation results compared with measured results are shown in Figure 6.

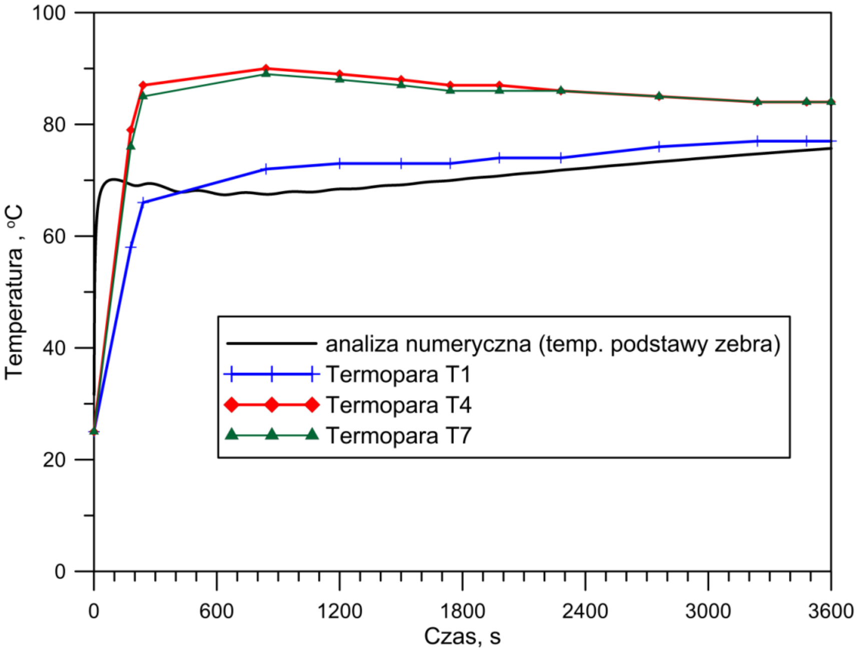

Figure 6. Changes in fin base temperature during cooling of cooling.

The results show very good agreement between the numerical modeling results and the experimental results. Experimental tests also confirmed that the developed exchanger could take all the heat from the minted molding mass and cool the mass in the expected time.

The research presented in the paper was carried out as part of the implementation of project NORW.19.01.01-12-0017/20.

Operando XRD studies and electrochemical properties of the Ni-rich $Li_{1.05}Ni_{0.905}Co_{0.043}Al_{0.052}O_2$ layered cathode material for the next generation Li-ion batteries

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Keywords: Ni-rich cathode materials, Li-ion batteries, operando XRD

ABSTRACT

Electrification of the transportation sector is nowadays regarded as one of the most promising solutions to address major energy and environmental issues associated with consumption of the fossil fuels [1]. Until now, considerable and successful efforts have been made to develop advanced electric vehicles (EV). However, the rapid development of EV industry has put forward much higher and strict requirements for the energy storage density and safety of the applied EV batteries. Obviously, the accessible to the driver driving range on one charge, as well as the charge time depend on the characteristics of the used batteries, which in turs depend mainly on the chemistry of the cells, i.e. choice of the cathode and anode materials, as well as the electrolyte.

To meet the demands of more than 500 kilometers driving range, high-energy-density cathode materials is required. As already presented in literature references, Ni-rich layered oxides ($LiNiO_2$-type) are expected to allow for a major breakthrough in construction of the high capacity and high power density cells, due to the very high reversible discharge capacity (>200 mAh g^{-1}) of the materials, high operating voltage (~3.7 V vs Li/Li^+), and relatively low costs. Nevertheless, such oxides still suffer from severe issues, such as surface sensitivity, poor structure with Li/Ni mixing effect, and insufficient thermal stability, which hinder their practical application [2]. In particular, presence of $LiOH/Li_2CO_3$ lithium residuals in the active material, which originate from the synthesis process, has deleterious effect on the rate performance and may affect cycling stability of the cells.

In this work, a simple vibratory dry mixing method was adopted to synthesize high Ni content $Li_{1.05}Ni_{0.905}Co_{0.043}Al_{0.052}O_2$ (NCA90) cathode material using the Ni-rich precursor $[Ni_{0.905}Co_{0.043}Al_{0.052}](OH)_2$ (ZhongWei). In the process, the precursor was mixed with $LiOH·H_2O$ (Sigma-Aldrich), with the assumed Li excess of 5 at.%. The mixture was calcined at 500 °C for 5 h in air, and then was calcined at 730 °C for 12 h under flowing O_2. The obtained NCA90 cathode material maintained the desired ball-like morphology of the precursor, and showed excellent electrochemical properties.

The electrochemical performance of the NCA90 cathodes was characterized using 2032 coin-type half cells with a Li metal anode and 1 M $LiPF_6$ in EC:DEC 1:1 vol. ratio electrolyte. To prepare the cathode layer, 80 wt.% of the active material, 10 wt.% of the Super P and carbon black additive (MTI), and 10 wt.% of PVDF (Arkema) were mixed, with NMP (Alfa Aesar) solvent added to obtain desired viscosity. Doctor blade was used to spread the slurry over Al foil. The layer was dried at 120 °C. A loading of the electrodes was about 4 mg cm^{-2} of the active material. The cycling tests were performed between 2.7 V and 4.5 V at a current density of 10 mA g^{-1} (0.05 C) for the first three cycles, and between 2.7 V and 4.3 V at a current density of 20 mA g^{-1} (0.1 C) for the subsequent cycles. The NCA90 cathode delivered an initial discharge capacity of 234.5 mAh g^{-1}at 0.05 C, with a capacity

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retention of 70.7% after 100 cycles.

To quantify the lattice volume changes during charge and discharge, operando XRD experiments were also conducted. A custom-made cell, having a Be window was used for the measurements. The X-ray diffractograms were measured in the 2θ range 15-75 deg. The loading of the electrodes was about 12 mg cm^{-2}. The applied specific current was 10 mA g^{-1} in the first cycle (up to 4.3 V), and 20 mA g^{-1} at the second cycle (up to 4.5 V). The registered charge/discharge curves, obtained using the operando cell, were nearly the same as those obtained using the normal 2032 coin type half-cell.

Analysis of the XRD operando data showed that the *a* lattice parameter of the *R*-3*m* symmetry decreases monotonically as the charging proceed, whereas the *c* parameter initially increases, and then begin to contract, for voltages higher than ca. 4.0 V. Above ca. 4.2 V, the *c* parameter abruptly decreases, which can be related to the so called H2→H3 phase transition. It is worth noting that this transition is responsible for the capacity fading, which is induced by the anisotropic lattice volume changes [3]. The exemplary contour plot in the selected 2θ range depicting changes of the 003 reflection during the first charge is presented in Figure 1.

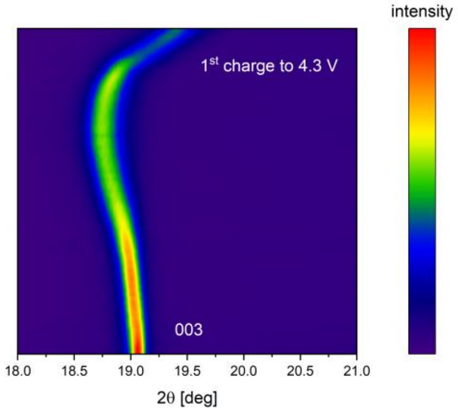

Figure 1. Changes of 003 reflection for NCA90 cathode recorded during operando XRD studies.

During discharge down to 2.7 V, the observed behavior is reversible, but showing small changes in the recorded intensity and position of the peaks. Overall, the generated profiles of the structural changes of the Ni90 cathode are almost symmetrical, with only small asymmetric behavior, especially visible during the first cycle. The results indicate that the operando XRD tests are important for realizing the real-time monitoring and provide on-site information of the structural evolution and phase transitions occurring for the cathode materials.

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Phytoremediation of post-industrial areas on the example of zinc heap Z.G. "TRZEBIONKA"

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Keywords: phytoremediation treatments, zinc heap, hazardous waste, arbuscular fungi

ABSTRACT

Europe where environmental pollution is a widespread problem. As a result of the extraction and deposition of materials and the emission of pollutants, the hydrographic conditions as well as the physical and chemical properties of soils change, which significantly affects their biological properties, causing changes in flora and fauna. As a result of the progressing industrialization, the concentration of many microelements necessary for life (copper, zinc, nickel, chromium) and other elements (lead, cadmium, arsenic, mercury) has increased significantly, which poses a great threat to the environmental balance. Human industrial activity increases the level of elements that harm ecosystems and pose a serious risk to living organisms.

The main purpose of the work was to prepare mycorrhizal strains of arbuscular fungi in order to increase the efficiency of phytoremediation of post-industrial areas. Research on the mycorrhizal status of plant species inhabiting selected degraded areas showed the presence of arbuscular fungi in the roots of all analyzed species. The isolation and identification of arbuscular fungi species and rhizobacteria related to the studied plants occurring in areas contaminated with heavy metals were carried out. Based on the research, a procedure was developed to improve the efficiency of phytoremediation treatments.

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Nanoframes-based catalysts for ethanol electro-oxidation in Direct Ethanol Fuel Cells

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Keywords: ethanol oxidation, nanocatalysts, durabillity, nanoframes

ABSTRACT

Direct ethanol fuel cells (DEFC) are a promising source of electric energy for many applications, e.g. mobile devices, drones, cars or boats. However, there are several major issues with anode catalysts used for ethanol oxidation reaction (EOR). Firstly, the costs of DEFC production are high because of the high price of platinum used as a typical anode catalyst. Secondly, the currently used catalysts have low selectivity for the complete oxidation of ethanol to CO_2 which lowers the efficiency of conversion of chemical energy to electrical energy. Thirdly, during the oxidation of ethanol by-products are formed, like acetic acid and acetaldehyde, due to the low selectivity of the catalysts. These compounds can cause poisoning of the anode catalyst, which reduces its catalytic activity. One possible solution to the above problems is to use as an anode catalyst so-called Pt-based nanoframes. Nanoframes differ from solid nanoparticles in that they are hollow inside, thus exhibiting better catalytic properties. It is possible to obtain nanoframes with different shapes, for instance triangular, cubic, octahedral, and decahedral. It is also possible to obtain nanoframes with different chemical compositions, e.g., PtNi, PdRh, or PtCu. The nanoframes have many advantages, among others, they provide many edges and corners, which are catalytically active due to the low coordination number of atoms on these edges and corners. Another advantage of the nanoframes is their high surface area to volume ratio, due to the removal of the non-functional atoms from the interior of nanoparticles. This operation not only improves the efficiency of catalytic reactions but also minimizes the usage of precious metals such as platinum, rhodium and gold.

Herein we present novel Pt-based nanoframes catalysts for the ethanol oxidation reaction. These nanocatalysts have an open 3-D structure, which provides a relatively high surface in comparison to nanoparticles with similar usage of Pt atoms. Moreover, presented nanoframes are covered with small (~ 3 nm) SnO_2 nanoparticles to enhance their catalytic performance, due to the so-called bifunctional. Obtained nanocatalysts were characterized by Transmission Electron Microscopy (TEM) combined with energy-dispersive X-ray spectroscopy (EDS) and X-Ray diffraction (XRD). Finally, nanoframes-based catalysts were tested electrochemically toward EOR.

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Compact electro-pneumatic linear drive prototype for air compression and expansion for use in compressed air energy storage system

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Keywords: renewable energy resources, CAES, linear expander/compressor, reverse operation, low pressure

ABSTRACT

The electricity generation by renewable energy sources (RES) like PV and wind turbines seems to meet the requirements of a modern energy policy in the field of economic, environmental, health and geopolitical [1]. However, due to the high unpredictability and inflexibility of electricity generation by those energy sources limits their applicable in domestic energy mix. The solution to ensuring the stability of electricity supplies from renewable energy sources is energy storage [2]. The technique specifies 3 methods of energy storage: electrical, mechanical, thermal [1,2]. Recognized technologies that can be successfully used in large scales and long work cycles of energy storage are hydro energy storage and compressed air energy storage (CAES). Current CAES solutions are characterized by large scales and high complexity [3,4]. There are no compatible and compact solutions for small renewable energy installations [5].

In this paper, we would like to introduce the idea of a compact micro CAES system based on a reversible linear machine, working in the compressor or expander mode [6]. A prototype of the technology was developed and tested so far in the expander operation mode. Figure 1 shows the construction of linear machine prototype.

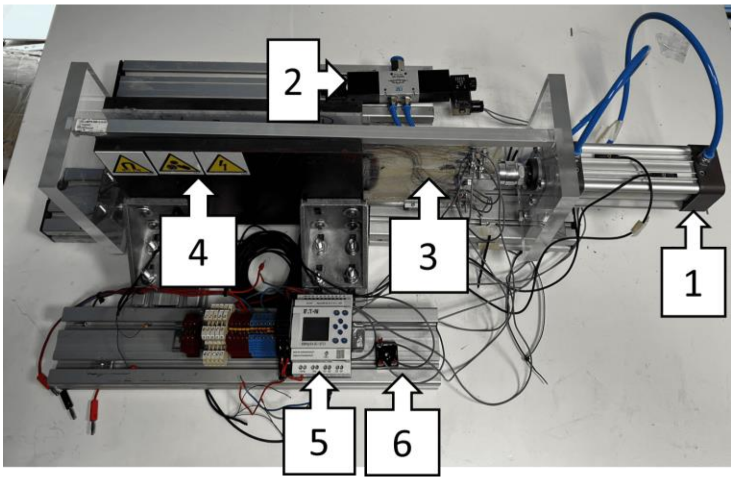

Figure 1. Prototype of linear expander/compressor. 1 – linear drive, 2 – directional control valve, 3 – coils, 4 - iron core with permanent magnets, 5 – programming logic controller, 6 – rectifiers bridge.

It contains of linear drive (1) with piston diameter 50 mm and stroke 100 mm, directional control valve (2), air coils composite (3) made of 6 coils with 32 turns each flooded in resin with wire diameter 1.3 mm, iron core (4) with 6 pairs of permanent magnets, Programming logic controller (PLC) (5), rectifiers bridge (6). In the compressor

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mode, the coils are supplied in the appropriate sequence which causes the piston movement and compress the air during reduced electricity demand. On the other hand, the expander mode converts the previously compressed air from the tank into electricity during increased electricity demand. As part of the work on the prototype, an analysis of the magnetic field was carried out.

Figure 2 shows the characteristics of open DC voltage and voltage-current for linear machine in expander mode.

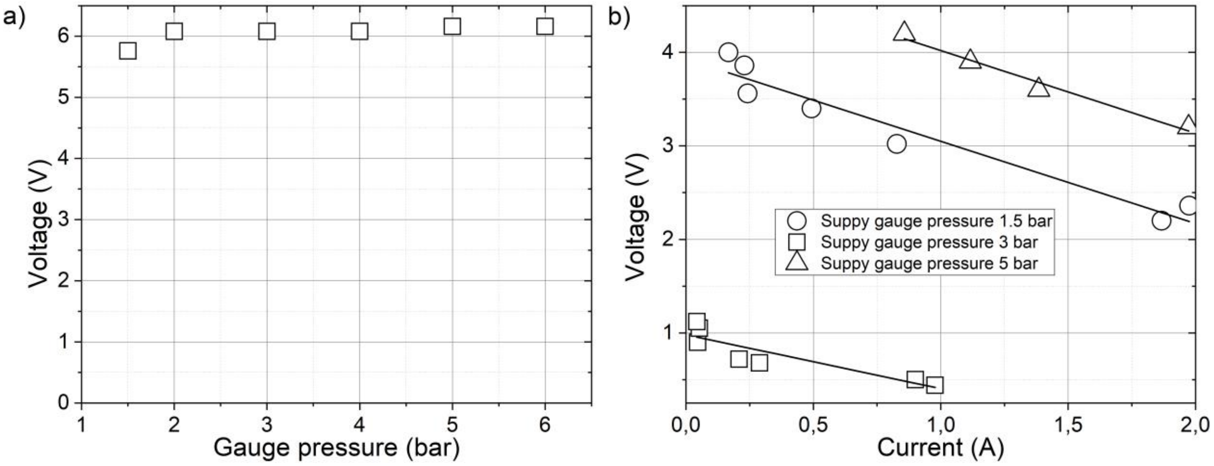

Figure 2. Characteristic of linear expander: a) Open DC voltage; b) Voltage-current.

In the expander mode, the prototype was supplied with compressed air with a gauge pressure in the range of 1.5 - 6 bar. The maximum voltage for all range was 6 V, due to the constant speed of the piston movement in the actuator resulting from the cross-sectional area of the inlet connectors. The maximum power obtained in the system was 4-6 W for gauge pressure of 3-5 bar. The small powers generated in the system result from too few turns of the coils, which results in low induced voltage and current values. In addition, the extension of the magnetic path along with the increase of the actuator stroke will result in higher generated powers.

The prototype is characterized by simplicity of construction, high resistance and compactness and can be used for micro CAES with a power of several kW. Its big advantage is the reversibility of its operation in the compressor-expander modes depending on the situation of electricity demand.

Acknowledgement

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Strategy for managing the flow of the gaseous medium in the measuring chamber of the gas calorimeter in order to reduce the gas temperature at the measuring point

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Keywords: non-normative fuels, calorimeter, heat of combustion, calorific value, excess air coefficient

ABSTRACT

The issue of the exploitation of gaseous fuels for the purpose of obtaining thermal energy dedicated to many industrial energy conversion processes is conditioned by physicochemical parameters reflected in the quality of the processes carried out. The current global situation in the distribution of gaseous fuels is highly monopolized. The gaseous fuel sector in the current energy structure of Europe is highly exposed to monopolistic activity, which, together with political activities, becomes a tool for forcing geopolitical changes on the European and world markets. Accordingly, many strategies for the production of energy from alternative gaseous fuels are being developed. These fuels include biogas obtained from the fermentation and decomposition of organic compounds, obtained in animal production, waste composting and municipal sewage treatment plants. The second source of alternative gaseous fuels are biomass and garbage gasification installations. The third source are installations implementing pyrolysis processes. The industrial application of these installations increases energy security, and their significance in this activity depends on the scale of the installations and input resources.

The processes of industrial production of alternative gaseous fuels are particularly dependent on the quality of the process input. This is especially true of gasification and pyrolysis installations where the feedstock is waste materials with different physicochemical characteristics and structures. The raw materials in these processes can be materials of natural origin such as wood, paper and other plant origin, and materials highly processed in chemical processes- plastics such as foils, oils, tires, etc. Such diversity, forces companies to segregate before the processing. Nevertheless, the input material still determines the quality of the gasification and pyrolysis processes carried out, which directly translates into the obtained fuel in the form of syngas. Its energy quality

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is closely related to the chemical composition, and it is closely related to the reactions taking place in the gasification or pyrolysis process. Therefore, it is necessary to constantly monitor the quality of the gaseous fuel obtained, in order to correct the processing processes as quickly as possible. Energy parameters of obtained gaseous fuel can be determined by using calorimeters. Measurement process realized by these devices depends on their construction and the specificity of the measurement method they carry out. Most of the gaseous fuels calorimeters on the market are dedicated for specified applications, e.g. for natural gas, propane-butane mixtures or biogas testing. Most often, these calorimeters analyze the chemical composition of the gas and based on the obtained result calculate the approximate calorific value of the gas. Currently, there are no widespreaded measuring devices on the market for testing the calorific value and the heat of combustion of gaseous fuels with a large range of changes in the chemical composition, which translates into various changes of the combustion process. Therefore, the authors proposed the concept of a gas calorimeter to determine the calorific value and heat of combustion of gaseous fuels with unidentified physicochemical parameters-non-normative fuels.

The concept of measurement and the concept of the device itself were developed [1, 2], which were verified in terms of theoretical aspects, in simulation tests and in preliminary laboratory tests. As a result of the conducted works, the information necessary to develop the final measurement structure of the device was obtained. One of the encountered measurement problems is the high value of the gas temperature in the measuring chamber in which the combustion process is carried out, which exceeds the permissible values for measurement with the use of thermocouples. Therefore, it was necessary to implement the concept of reducing the temperature value by changing the share, in the measurement process, of the air mass stream, supplied as a factor heated by the flame from the combustion of gaseous fuel. The modification allows to change the temperature of the gases obtained in the measuring chamber, and the entire process is additionally controlled by measuring the excess air coefficient with the use of an oxygen sensor. The automation of the process, depending on the temperature value measured with a thermocouple together with the measurement of the oxygen concentration in gases in the measuring chamber with the simultaneous control of the mass flow of the supplied air, required the development of a gas flow management strategy in the calorimeter measuring chamber. This strategy was verified in simulation studies with the use of numerical tools. The obtained results are presented in the following article.

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Industrial implementation of high-temperature nitrous oxide decomposition technology in nitric acid plants

Marek Inger[1,*], Monika Ruszak[1], Jakub Rajewski[1], Magdalena Saramok[1], Artur Olszak[1], Paweł Capała[1], Wojciech Kowalik[1], Marcin Wilk[1]

Keywords: greenhouse gas, N_2O abatement, nitric acid

ABSTRACT

The nitric acid plants are one of the largest stationary sources of greenhouse gas emission - nitrous oxide (N_2O). The applicable emission standards and a high price of emission allowances are an effective incentive, forcing nitric acid producers to invest in technologies to reduce nitrous oxide emissions. Currently, a technology widely used on an industrial scale is a high-temperature N_2O decomposition (HT-deN_2O). It is based on the catalytic decomposition of nitrous oxide from the stream of post-reaction gases after ammonia oxidation. Typically, HT-deN_2O catalyst is installed in the ammonia burner, below the catalyst gauzes package. Due to the demanding process conditions, it must meet the following requirements: efficiently decompose N_2O at a high catalyst load (GHSV=50,000–200,000 h^{-1}), ensure a long time of operation under extreme hard conditions (T=850–920°C, high concentration of water vapour), be inactive towards the main product of ammonia oxidation – NO, show a high mechanical strength and abrasion resistance.

Łukasiewicz-INS has developed [1], produces and successfully implements its own catalyst for N_2O decomposition (PKR) on an industrial scale.

Many years of experience in using the PKR catalyst in ammonia burners show that, apart from the typical catalytic features, the operating conditions are of great importance. The high reaction temperature requires the use of a special supporting structure for the catalyst layer – i.e. catalytic basket. Under operating conditions, deformation of the catalytic basket and migration of the catalyst layer may occur. As a consequence a gas flowing through the catalyst layer may be by-passed, which adversely affects the final N_2O reduction. Based on the experience gained, some solutions have been developed to minimize the unfavorable phenomena occurring during catalyst operation, which may cause a higher N_2O emission than that resulting from the catalyst properties. A method for stabilizing the catalyst layer in ammonia burner [2] and methods of sealing the catalyst basket to prevent leakage and gas by-passing [3,4] were developed.

As a result of using PKR catalyst, N_2O emission is reduced by over 90%. Proprietary solutions for the construction of the catalytic basket, successfully used in nitric acid plants, effectively reduce the occurrence of undesirable phenomena and guarantee stable operation of the catalyst, and in some cases increase the reduction of N_2O emission to over 95%.

[1] Patent PL no. 207 666.
[2] Patent PL no. 236 239.
[3] Patent PL no. 236 238.
[4] Patent PL no. 236 240.

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Study on co-combustion process of H_2/CH_4 mixtures in high-temperature thermal processes

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Keywords: hydrogen, decarbonisation, thermal processes, nitric oxide

ABSTRACT

The economic development that has been taking place over the past decades, combined with the growth of the world's population, have contributed to a sharp increase in energy consumption. Currently, fossil fuels are the dominant energy source in the energy market. This state of affairs has a very negative impact on the environment, contributing to the continued increase in greenhouse gas emissions and air pollution [1]. The main industries responsible for the largest share of greenhouse gas emissions are steel (6.2%), cement (3%), petrochemicals (3.6%), chemicals (2.2%) or non-ferrous metal production (about 1%). The mentioned production processes are characterized by a high rate of energy consumption, directly related to the need for high process temperatures, well above 1270 K in many cases. This situation makes it necessary to look for new solutions to decarbonize production processes.

The dominant trend is to replace both, electricity and heat produced from fossil fuels, with energy from renewable sources. This is particularly advantageous for electricity generation, such as with photovoltaic panels or wind power. Unfortunately, in the case of thermal energy, especially in high-temperature processes, solar or wind energy is not directly feasible.

One possible solution is to replace fossil fuels with alternative fuels derived from the processing of renewable energy resources. Among the new fuels are hydrogen, ammonia, biogas and synthetic gas such as green methane.

Hydrogen-based thermal energy production is the cleanest among the alternative energy sources, because hydrogen combustion product is only water vapor, making it possible to achieve zero greenhouse gas emissions [2, 3]. However, hydrogen, as a gaseous fuel, has significantly different physico-chemical properties, compared to natural gas, which is commonly used in the previously mentioned high-temperature processes. In the gas phase (as used in industry), hydrogen has more than three times lower calorific value, while the speed of flame propagation is about 7 times higher. The adiabatic flame temperature of H_2 combustion in air is higher than for hydrocarbon fuels by about 140 to 170 K. (in range of Φ=0,55-1,10) [4]. The flammability limits of hydrogen are much wider, which offers better stability of combustion processes within the wide limits of combustible mixtures. Changes in the physicochemical properties of fuels have a direct impact on the combustion process, including the emission of toxic compounds (NO, CO, HC), but also on the heat transfer process in the combustion chambers, which has a consequent effect on the efficiency of the technological process.

The article presents the results of a study of the co-combustion process of methane and hydrogen with volumetric shares of up to 50%, which corresponded to 23% of the energy share of hydrogen in the mixture with methane. Experimental tests were performed for three different combustion system configurations, possible for industrial thermal power generation systems: a diffusion burner (Fig. 2a), a mixed system (Fig. 2b) and a system in which hydrogen was introduced by independent nozzles located at a 3D distance from the burner axis (Fig. 2c). In addition, due to the fact that in industrial high-temperature processes very often the air is heated (in the regeneration process), the tests also included increased air temperature, which was up to 720 K.

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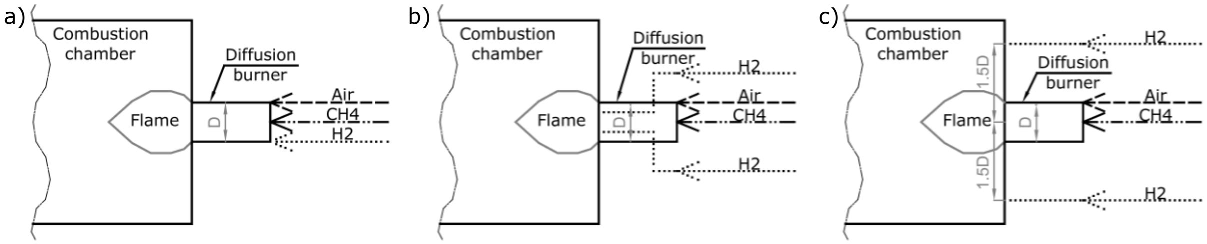

Figure 2. Configuration of the combustion systems: a) diffusion burner, b) diffusion burner with hydrogen supply nozzles inside – mixed system, c) independent hydrogen injection by nozzles located outside the burner at a distance of 3D.

The research work was carried out for a fixed burner power of P=100 kW, for a wide range of equivalence ratio values from 0.47 to 0.97. This allowed testing of combustible mixtures from approximately stoichiometric mixtures to lean mixtures.

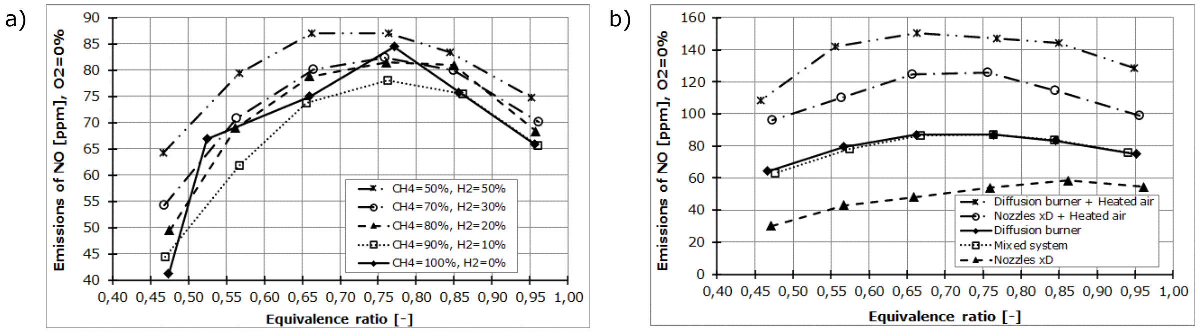

Figure 2. Emission of nitrogen oxides depending on the equivalents: a) in the case of a diffusion burner, b) in the case of a mixture with a volume fraction of 50% H_2 with CH_4

The results obtained for nitrogen oxide emissions showed that for the base case (diffusion flame Fig. 3a), increasing the share of H_2 in the fuel increases emissions. This is a consequence of the increase in the flame temperature, and thus an increase in NO emissions formed according to the thermal mechanism especially for oxygen-rich mixtures. Similarly, an increase in emissions due to an increase in flame temperature was noted for tests in which the oxidizer was preheated (Fig. 3b). The lowest nitric oxides emissions was measured for the combustion system, where H_2 was injected into the combustion chamber through nozzles placed at a 3D distance from the burner axis. This has resulted in a more uniform temperature distribution throughout the entire volume of the combustion chamber and further increases exhaust gas recirculation. It reduces the occurrence of oxygen-rich areas and hotspots, where nitrogen oxides are more intensely formed. The achieved uniform temperature distribution also improves the heat transfer process inside the combustion chamber. During the tests, for analysed combustible mixtures, combustion instabilities were not observed. Increasing the share of H_2 in the fuel resulted in a slight shift of the area of highest temperatures toward the burner outlet. The results showed that it is possible to co-combust H_2 and CH_4 in semi-adiabatic combustion chambers in industrial high temperature applications.

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Compositionally complex materials for electrochemical applications

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Keywords: high-entropy oxides, mixed conductors, proton conductors

ABSTRACT

Many groups of oxides may form so-called compositionally-complex oxides (CCO), high-entropy oxides (HEO) or entropy-stabilized oxides (ESO). So far, there have been published only a few reports dealing with the electrical properties of these complex materials. They showed either higher [1] or lower [2] electrical conductivity in comparison with low-entropy oxides of the same structure. These pioneering works started the research on electrical properties of CCOs but there is a lack of fundamental understanding of both transport processes and electrochemical properties of these systems. Gaining deep knowledge on these materials will enable fine-tuning their functional properties suitable for energy conversion by means of electrochemical devices.

The electrochemical and transport properties of oxide are determined by the mobile electronic (holes/electrons) and ionic charge carriers. In the case of compositionally-complex oxides little is known on the types of charge carriers contributing to the total conductivity. The first assumption which could be considered is that they are mixed ion-electron conductors with ion charge carriers being both oxide ions and protons. The presence of at least five cationic constituents, related to that disorder, strain and lattice distortions may be expected to influence both concentration of particular charge carriers and their mobility.

In this work, selected properties of multicomponent oxides based on well-known proton-conducting systems, namely barium zirconate perovskite and lanthanum niobate fergusonite are presented and discussed. In particular, structural, thermogravimetric, and charge transport properties are showed. Special attention was focused on the properties related to proton conduction.

The ABO_3 and ABO_4 oxides in which either the B- or the A-cation sites are occupied by 5-10 different cations were synthesized by a high-temperature solid-state route. The oxides designed as electrolytes contained up to 50 % acceptor constituents, whereas these planned as electrode materials contained transition metal cations (e.g. Fe). Structural properties were studied by X-ray diffraction (XRD) using a Philips diffractometer and high-temperature X-ray diffraction (HT-XRD) with Anton Paar HTK 1200N camera. Formation of proton defects was studied with thermogravimetry (TG) using Netzsch STA 449. Electrical properties of the high-entropy oxides were studied by electrical impedance spectroscopy (EIS) using Gamry 3000 potentiostat. For selected samples, the conductivity relaxation experiments were performed.

It was showed that in both groups of complex oxides, in the humidified atmosphere, proton defects form. The highest content of proton defects (0.212 mol/mol) was found in $BaZr_{0.1}Sn_{0.1}Ti_{0.1}Hf_{0.1}Ce_{0.1}Y_{0.1}In_{0.1}Sm_{0.1}Yb_{0.1}Zn_{0.1}O_{3-\delta}$, while in the fergusonites, the highest proton defect content was 0.01 mol/mol. Despite so large difference in proton defect content, the electrical conductivity in both material groups is significantly higher in humidified atmosphere than that in dry one. Figure 1 shows exemplary results of temperature dependence of total conductivity in the ABO_3 and ABO_4 oxides.

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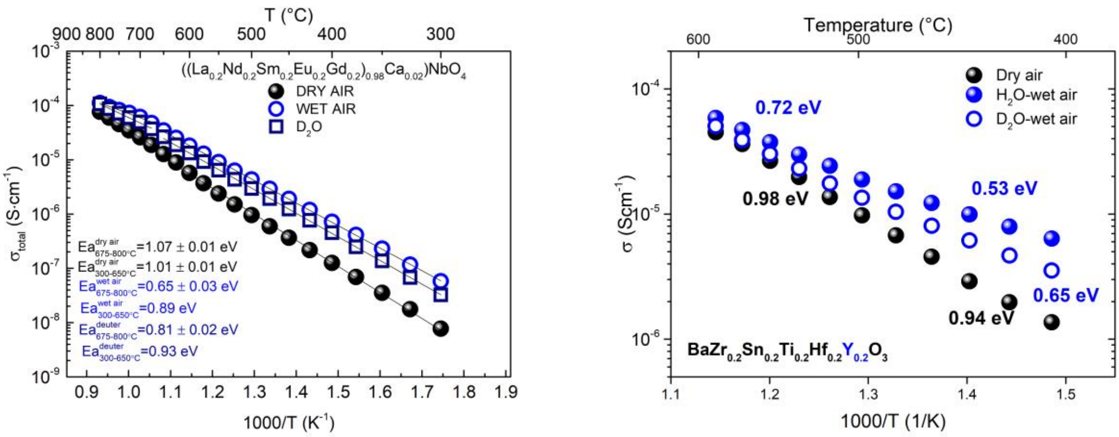

Figure 1. Temperature dependence of total conductivity in the Ba(Zr,Hf,Ti,Sn,Y)O_3 and (La,Nd,Sm,Eu,Gd)$_{0.98}$Ca$_{0.02}$NbO$_4$ oxides.

Based on the activation energy of conductivity, the influence of cationic disorder present in compositionally complex oxides designed as electrolytes on the mobility of proton charge carriers is discussed. First of all, it is assumed that the anionic lattice, with the exception of point defects, in an HEO is ordered [3]. On the other hand, the presence of disorder in the cationic sublattice, causing a distribution in cation-oxygen bond lengths and strain, inevitably introduces a disorder into the oxygen sublattice. The disorder in the cation sublattice may also decrease the tendency to defect clustering. Electrical properties of the mixed-conducting complex oxides is discussed.

Acknowledgements

The research was financially supported by the National Science Centre (NCN), Poland, within the project 2019/35/B/ST5/00888.

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Effect of bedrock on the content of naturally occurring radionuclides in soils

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Keywords: naturally occurring radioactive material, geology, public health, radioecology

ABSTRACT

Naturally occurring radionuclides of terrestrial origin are present in almost all environmental media. There are many different radioisotopes, but in practical terms only a few have sufficient abundance and radiological importance [1]. Among these isotopes should be mentioned the primordial ^{40}K and series of ^{238}U, ^{232}Th. The potassium radioisotope is the most common element and usually has the highest value of radioactivity. It is caused by the constant ratio to the potassium element, which is the seventh component (2.83%) of the weight content in the Earth's crust [2]. However, less concentrated uranium and thorium have a higher radiological impact, which is connected with a series of decays, generating also more harmful alpha radiation. Possible routes of population exposure to terrestrial radionuclides contained in soils are as follows: direct exposure to external radiation, internal radiation from inhalation of airborne radionuclides, and internal dose from ingestion (food and water contamination) [3,4]. This study focuses exclusively on radionuclides from the former source, where the radiation dose comes from gamma and beta radiation connected with the presence of radionuclides in the surface soil layer. It is possible to calculate the dose for the population, based on the concentration in the soil of mentioned radioisotopes. However, a key issue for a proper assessment of radiological exposure at the local scale is the selection of measurement points. It is crucial to obtain a statistically valid sample to avoid overestimation and underestimation errors. The distribution of sampling points based on a uniform spatial distribution does not reflect the actual condition due to local factors. Among others, the varied geology of the terrain has a significant impact.

Therefore, this work aimed to show the applicability of geological studies to the investigation of the radioactivity of radionuclides of terrestrial origin in the soil. Soil samples were taken from a Tatra Mountains area for which geological maps were available. The concentration of selected radionuclides incl. ^{40}K, ^{238}U, and ^{232}Th was determined by gamma-ray spectrometry with HPGe-detector. Putting the research in the context of public health, the results obtained were also calculated in terms of the adsorbed dose rate. Radioactivities and calculated absorbed dose rates were co-related to complex bedrock matric based on an original methodology.

To correlate the extracted soil profiles with the bedrock, the cartographic study "Detailed geological map of the Tatra Mountains on a scale of 1:10,000" was used [5]. The WMS (Web Map Service) server was used, and spatial data were processed in ArcGIS, a specialistic software for GIS data analysis. Geoprocessing tools were used for automated spatial analysis of the study areas. The results obtained were matched with geological data based on GPS coordinates. However, considering that the process of soil formation is not limited to direct contact and is also affected by the surrounding geomorphology, a broader analysis of the bedrock composition was performed including neighborhood areas. The analysis area was limited to 0.5 km^2 for each point.

In order to find correlations between composition of bedrock and the soils' radioactivity, the Principal Component Analysis (PCA) was performed. PCA was carried out for 11 complete standardized cases using Statgraphics Centurion 18 software. For chemometric

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analysis, individual components of the bedrock have been grouped, as shown in Figure 1. Groups were created based on similarities derived from the PCA analysis for each of the parameters and gathered to increase the clarity of a biplot (Fig. 1).

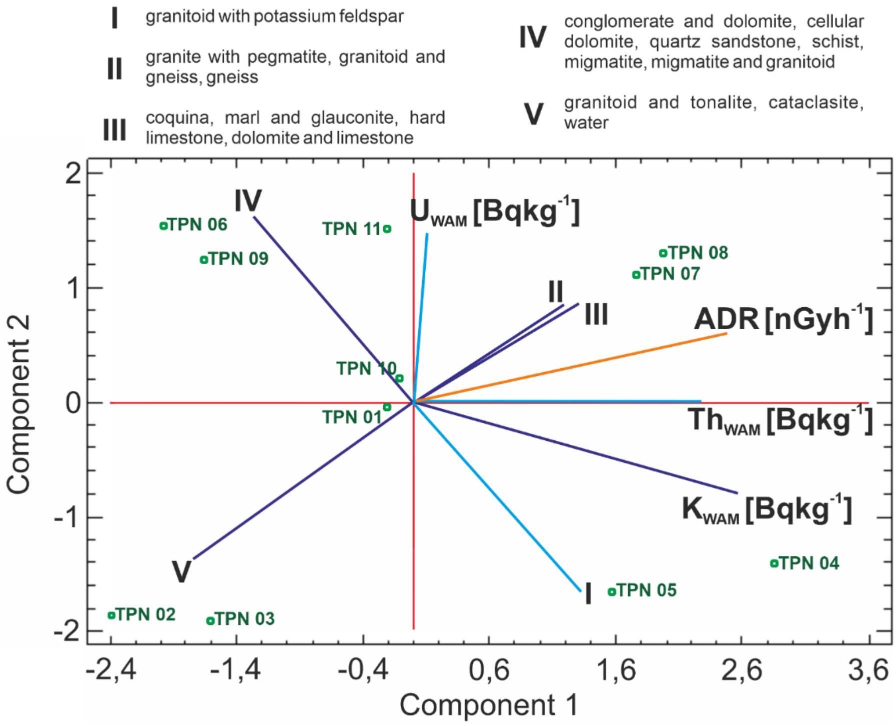

Figure 1. Biplot - Principal Component Analysis

Some correlations were observed between the content of specific rocks in the bedrock layer assigned to the area of the sampling point. The limitation to 0.5 square kilometers in the analysis of the bedrock that resulted from the assumption, seems to have found the right approach. Confirmation of this thesis appears to be provided by including in the analysis, e.g., the water reservoirs, the shares of which proportionally reduced the coefficient of ADR. The relationship seems obvious, however, it shows the impact of reducing a zone of bedrock, of which soil is the product of weathering processes.

The rocks that significantly affected the absorbed dose rate of soils were strongly related to the radioactivity of the uranium series, and these were the following rocks: Granite with pegmatite, gneiss, granitoid and gneiss, coquina, marl and glauconite, hard lime-stone, dolomite and limestone. The rock types additionally showed good correlation with isotopes of the thorium series. Strong complicity with both uranium and thorium series was reflected in the highest ADR. Granitoids with potassium feldspar, on the other hand, contributed the largest share of ^{40}K isotope content.

In summary, the proposed methodology is especially applicable to research groups that are not experts in geological science, since it uses only raw data provided by national geological institutions. The study area is used only as an example, but the procedure could be widely applied. Only one requirement is to have access to geological data.

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Status of Renewable Energy Systems in the World and Prospects

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Keywords: Renewable energy, solar termal, photovotaics, wind energy, biomass

ABSTRACT

This presentation examines the current status of renewables in the world. The presentation starts with some facts about climate change, global warming, and the effects of human activities, such as the burning of fossil fuels on the climate problem. It then outlines of the status of renewables in the world, which includes their shares with respect to conventional fuel use for power and for electricity production alone, and their social dimension in terms of jobs created. Then the basic forms of renewables are examined in some detail, which include solar thermal, both for low and high temperature applications, photovoltaics, hydro power, onshore and offshore wind energy systems and biomass/biofuels. In all these the basic technology is presented followed by the current status, the installed capacity in the last decade, which reveals their upward trend, as well as the prospects of the technology and some new research findings.

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The impact of CO_2 on the population of mold fungi in the outdoor air and closed spaces in terms of climate change

Dorota Koruba[1,*]

Keywords: climate change, carbon dioxide, mold fungi, mycotoxins, indoor air quality.

ABSTRACT

Climate change involves changes in the concentrations of greenhouse gas emissions (carbon dioxide, methane and nitrous oxide), temperature increases, rainfall patterns, extreme weather events and radiation. The increase in global temperature at the end of the 21st century is likely to be 1.5°C to 4.5°C. [1]. In 2014 the report "Climate Change 2014 ..." presented abundant evidence of a strong, coherent, almost linear relationship between cumulative CO_2 emissions and the global temperature change that is predicted to take place by 2100. A large proportion of anthropogenic climate change resulting from CO_2 emissions is irreversible on a scale from centuries to millennia. As a result of human activity, we observe progressive changes in the climate**.** Anthropogenic greenhouse gas emissions are caused by economic activities, mainly the burning of fossil fuels (such as coal, oil and natural gas). The aforementioned changes in climatic conditions are likely to affect the population of mold fungi.

The paper presents two aspects of the impact of mold fungi on the human population. The first aspect concerns the global impact of mold fungi on the contamination of crops with mycotoxins in terms of climate change. In areas where droughts occur, along with high temperatures caused by an increase in CO_2 concentration, they increase the production of aflatoxins [2]. Of the four different aflatoxins (B1, B2, G1, G2), aflatoxin B1 (AFB1) is the most dominant and has the highest toxicity. It has been classified by the International Agency for Research on Cancer (IARC) as a known human carcinogen [3]. The literature states that the greatest risk of aflatoxin contamination concerns the cultivation of corn and nuts, peanuts, pistachios and cotton, as well as cereals.

The second aspect of the effects of mold fungi and CO_2 concentration concerns their influence on people staying in closed spaces.

The paper presents the results of field and laboratory tests on indoor air quality (identifying species of molds, microclimate parameters, with particular emphasis on CO_2), taking into account the autumn and winter period in living quarters.

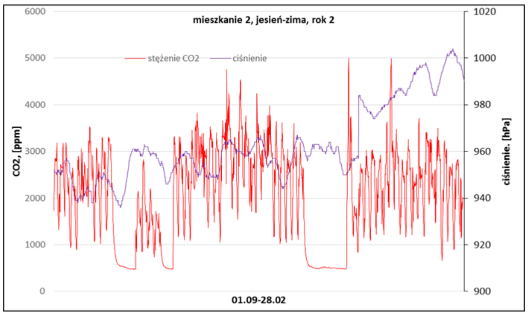

Fig. 1. Graph of CO_2 concentration in the air and air pressure - flat (autumn-winter).

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The results of laboratory tests on the effects of CO_2 (CO_2 concentration = 5000ppm) on mold fungi are also presented, which document information about morphological changes and adaptation of mold fungi to changing environmental conditions (fig.2)

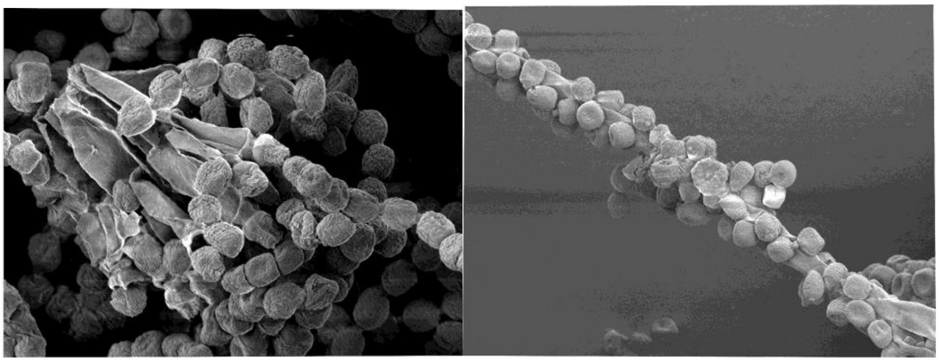

Fig. 2. Penicillium spp. - growth in an atmosphere of CO_2 = 5000ppm. (area x 3500) - picture 1 and Penicillium spp.- growth in the atmosphere of CO_2 = 400ppm. (area x 2500) - picture 2.

The paper also presents the impact of mold fungi and CO_2 on human health.

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Investigation about Combatting Naphthenate Fouling in Oil and Gas Facilities

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Keywords: demulsifier, naphthenates, chemistry, oil production

ABSTRACT

Naphthenate deposits are salts of metals and naphthenic acids. They can appear during crude oil exploitation, especially in high TAN crude oils, containing high amount of water. Usually, the amount of naphthenic deposits increases with the water content in the oil. After the reaction between naphthenic acids and metal salts (mostly calcium salts), the deposit can be created, especially in production separators, what causes problems during production processes. This deposit (naphthenates) is hardly soluble in water and usually floats below oily layer. Standard methods include lowering pH with acids that react with naphthenates, what creates other, water-soluble salts, like acetic acid. Nevertheless, use of acids can create corrosion. That is why it is beneficial that novel naphthenate inhibitors do not contain these types of chemicals. Other surfactants are now effectively used to achieve excellent inhibition properties.

In Europe, the problem is the most common on oil rigs in Norway and United Kingdom, nevertheless, it is also common in African countries, i.e. Angola and Nigeria. Many tons of chemicals are used to combat naphthenate deposition, usually by inhibit its' creation, but also, sometimes, it is necessary to dissolve the scale that precipitates in time. The presentation is about the characteristics of naphthenate fouling, historical ways to inhibit them and current attitudes to the problem, together with laboratory testing of the naphthenate inhibitors and solvents, including authors' work in the laboratory in Poland and oil rig in Angola, basing on currently known knowledge and standards. Moreover, the attitude towards less toxic chemical products will be taken into account, basing on literature and investigations taken by the authors.

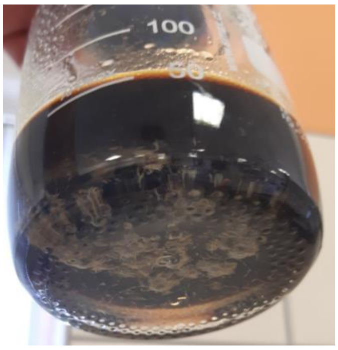

Figure 1. Naphthenate deposit under oil layer [photo M.Korzec]

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Novel catalyst for more efficient H_2 production via water-gas shift

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Keywords: hydrogen, water-gas shift, catalyst, pilot plant test

ABSTRACT

Despite enormous efforts focused on a technologies of green-H_2 production an intense investigations to decrease energy consumption and pollutants emissivity of conventional large-industry grey-H_2 and syngases technologies are still carried out. The improvement of well-known catalysts and a development of new-generation catalytic systems remain very important elements of strategy to meet environmental and technological requirements [1].

The catalytic water-gas shift ($CO + H_2O \rightleftarrows CO_2 + H_2$) is one of the most basic processes of obtaining hydrogen in various brands of industry. The catalyst applied to run this reaction is one of the crucial factors determining the efficiency of industrial-scale process of H_2 production. A join research carried out by Łukasiewicz – INS and Grupa Azoty S.A. are focused on a new-generation catalyst for low-temperature water-gas shift (LTS). The main goal is to design a highly active catalyst of favorable mechanical parameters (crushing strength, bulk density etc.), improved thermal stability and series of other properties which enables thermodynamically beneficial long-term performance in a low-temperature range.

This contribution reports the results of complex investigations toward modified CuZnAl catalysts design (optimization of catalytic material recipe and shape of catalyst formed), scaling-up the catalyst production technology and the effect of catalyst trial charge operating in WGS section of NH_3 plant (Fig. 1).

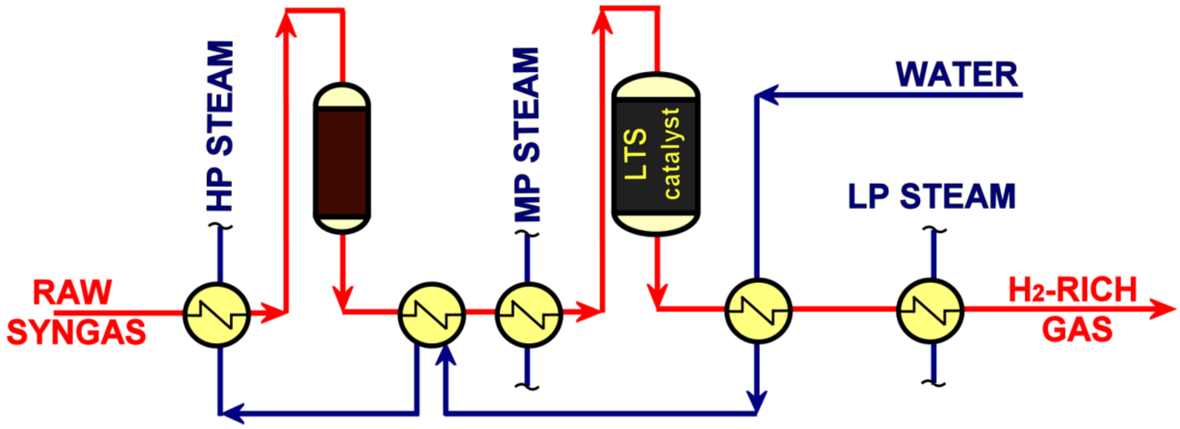

Figure 1. The scheme of WGS section in H_2-rich synthesis gas plant.

The operating experience of the trial charge to date indicates very good performance the new catalyst. The future application of a new catalyst with a modified formula and appropriate shape in H_2 and H_2-based chemicals plants may contribute to the improvement of the energy demand of the entire production process.

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Acknowledgments

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Russian supplies of energy resources on world markets

Piotr Kwiatkiewicz[1]*

ABSTRACT

The energy resources of the Russian Federation are the country's guarantee of a strong position in the global industry markets. These reserves are a component of every mid- and long-term forecast of consumption and prices: carbon, crude oil, and natural gas. The role of the depository of the world's reserves of fossil fuels is not the only one played by the Russian Federation. Currently, it is also a producer and, due to the country's own limited consumption, the leading exporter thereof. For years it has been the largest supplier of hydrocarbons in world trade and there are no indications that the situation could change in the foreseeable future.

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Development of new copper-contained perovskites $La_{1-x}Sr_xNi_{1-y}Cu_yO_{3-\delta}$ as air electrode materials for boosting the performance of reversible SOCs

Jakub Lach[1], Kun Zheng[1,2]*, Ryszard Kluczowski[3], Konrad Świerczek[1,2], Anna Niemczyk[4]

Keywords: copper contained perovskite, air electrode material, Reversible Solid Oxide Cell

ABSTRACT

Various alternative energy storage technologies are under development to balance the supply-demand mismatch of renewable energy sources, such as solar and wind sources, which are characterized as intermittent power and strongly related with many factors including weather changes or geographic location. Reversible Solid Oxide Cells are one of the most promising energy storage and conversion devices, which can be successfully scaled up for the decentralized energy storage and conversion applications. Reversible SOCs possess the capability of generating electrical energy and heat by utilizing chemical energy of fuel, and storage of surplus electrical energy in the fuel within the reversed operation mode. Effectively working air electrode with a high efficiency of oxygen reduction and oxygen evolution reactions is indispensable to guarantee the high and stable performance of reversible SOCs. Furthermore, fuel electrode-supported cell design allows to significantly reduce the cell's ohmic resistance and maximize the electrochemical performance. The majority of developed air electrode materials for SOCs present either perovskite-type ($ABO_{3-\delta}$) or perovskite-related crystal structure, which is principally associated with a wide range of available chemical compositions, enabling to design and obtain desired structural, thermomechanical and mixed ionic-electronic transport properties [1-3].

In this work, $La_{1-x}Sr_xNi_{1-y}Cu_yO_{3-\delta}$ perovskites were evaluated as very promising air electrode materials for reversible fuel electrode-supported SOCs. Physicochemical properties regarding crystal structure, thermal expansion properties, oxygen content change vs temperature of the studied oxides, as well as the electrochemical performance were systematically investigated.

The room-temperature phase of the obtained $La_{1-x}Sr_xNi_{1-y}Cu_yO_{3-\delta}$ (x = 0-0.1, y = 0.25 and 0.5) materials is classified to the trigonal system with *R*-3*c* space group, and phase transitions from *R*-3*c* to simple perovskite *Pm*-3*m* have been recorded by HT-XRD studies. The thermal expansion of considered oxides is found to be anisotropic, and the TEC values are very close to the commonly used electrolytes (e.g. 12.7×10^{-6} K^{-1} for $La_{0.95}Sr_{0.05}Ni_{0.5}Cu_{0.5}O_{3-\delta}$). Doping with strontium in the A-site significantly increases the oxygen non-stoichiometry. The investigated materials are stable and compatible with GDC-10 and LSGM electrolytes. The selected material is applied to construct full anode-supported SOFC, and an excellent power output is recorded with 445 $mW\cdot cm^{-2}$ at 650°C in wet hydrogen (Fig. 1), and the reversible operation of cells has also been conducted.

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The results indicate that studied perovskites can be considered as stable air electrode materials for fuel electrode-supported SOCs, allowing to obtain excellent electrochemical performance in the reversible operation.

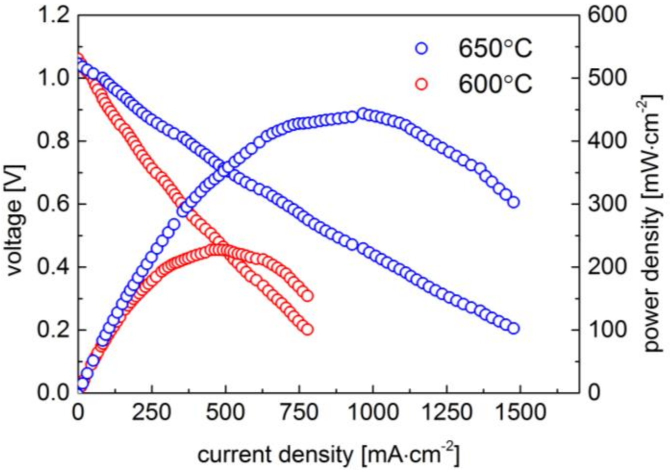

Fig 1. The performance of anode-supported SOFC in the humidified hydrogen.

Acknowledgment

This project was funded by the National Science Centre, Poland, on the basis of the decision number UMO-2020/37/B/ST8/02097. K. Zheng and K. Świerczek acknowledge financial support from AGH University of Science and Technology under grant no. 16.16.210.476.

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Preparation of porous silicon carbide for energy applications

Katarzyna Lejda[1,]*, Weronika Pazdyk[2], Honorata Osip[1], Cezary Czosnek[1]

Keywords: silicon carbide, carbonizates, waste wood, energy

ABSTRACT

Silicon carbide SiC due to excellent physical and chemical properties finds numerous applications in many fields of technology. The high thermal conductivity, combined with the resistance to radiation damage, contributed to its use in nuclear power as a material for multilayer coating of nuclear fuel particles. Good thermal conductivity and chemical resistance offer new application possibilities as catalyst carrier in some high-temperature reactions, such as the production of synthetic methane. The chemical resistance of SiC at high temperatures, combined with a relatively low density, in turn, makes it possible to use it as a filling material for volumetric receivers in solar thermal power plants.

Silicon carbide is obtained mainly by carbothermal reduction of silica SiO_2 (Acheson process). Depending on the type of starting materials used, there are many modifications to this process. This work presents a study on the preparation of porous silicon carbide from wood-based waste in a system with liquid oxygen-bearing organosilicon compounds (source of silica) using the two stage method. In the first stage, wood-based waste was pyrolyzed at a temperature of 1300 °C in an argon atmosphere. The obtained porous carbonizates were subjected to several impregnations with liquid organosilicon precursors followed by thermal treatment under argon flow. The final temperature of the second stage was 1550 °C and ensured an efficient course of carbothermal reduction of silica to silicon carbide. The final C/SiC composite materials were characterized with FT-IR spectroscopy and powder XRD. The morphology of the composites was examined by scanning electron microscopy SEM. The textural properties were tested by low-temperature nitrogen sorption.

The obtained C/SiC composite materials retained the cellular structure of the wood with relatively large specific surface areas.

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Methane conversion with carbon dioxide over CNT supported catalysts

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Keywords: dry reforming of methane, carbon nanotubes, ceria, platinum, RWGS

ABSTRACT

Dry reforming of methane (DRM) converts two greenhouse gases, CH_4 and CO_2, into syngas ($CO+H_2$). The reaction is endothermic and is usually carried out at above 800°C over transition and noble metals supported on such oxides as Al_2O_3, MgO, SiO_2, CeO_2, ZrO_2, etc. The most widely used active phase is Ni, which is abundant, inexpensive, and unfortunately - prone to carbon deposition. To improve the resistance of the catalyst to coke formation it is important to properly select the active phase (e.g., by creating the bimetallic systems), the support and promoter. Moreover, it is important to apply the efficient method of catalyst preparation that will result in good metal distribution over the support and in the formation of the strong metal-support interaction (SMSI). Incorporation of Pt to Ni catalysts was found to inhibit carbon formation during DRM [1]. The modification of the electronic structure of active sites in bimetallic catalysts influences the activation energy of CH_4 dissociation and CO_2 activation. Moreover, it improves the reactivity of surface oxygen that are used for suppression of surface carbon species. According to [2] Pt-Ni weakens the hydrogen dissociation decreasing the occurrence of the reverse water gas shift reaction (RWGS) and increasing H_2 production. Reduced C deposition during DRM can be also achieved by using a promoter that delivers basicity to the catalyst. One of the oxides that can be used in the catalytic system for DRM is the cerium oxide (CeO_2) and mixed cerium-zirconium oxide ($CeZrO_2$) that show very high resistance towards carbon formation [3]. Lanthanum oxide (La_2O_3) incorporation to the catalyst was also found beneficial [4].

In this work the CNT supported Ni and Pt-Ni together with $CeZrO_2$ (CeZr) and La_2O_3 (La) were obtained using different metals salts and syntheses parameters. The syntheses were conducted via co-precipitation in the hydrothermal conditions. The aim of the work was to obtain the nanosized, well-dispersed bimetallic catalysts characterized with strong metal-support interaction to improve their performance in DRM. The obtained catalysts were characterized, e.g., by using XRD, N_2 sorption, TEM and SEM with EDX, and tested in DRM under the excess of CO_2 at temperatures ranging from 450 to 900 °C.

Fig. 1 present the results of microscopic observations of the Pt-Ni-$CeZrO_2$/CNT catalyst. The selected area diffraction (SAED) proved the formation of $CeZrO_2$ and the Pt-Ni alloy. The size of the crystallites of active phases deposited uniformly over CNTs was less than 5 nm. Fig. 2 shows the performance of catalysts in DRM. They were found to be active in the DRM even from 600°C and resistant to C deposition (thanks to the dissociation of the excess CO_2 on the oxygen vacancies in the $CeZrO_2$ or La_2O_3). The catalyst composition and the interaction between different phases was found to have strong impact on substrates conversions. For example, the presence of Pt-Ni alloy significantly increased the contribution of RWGS during DRM.

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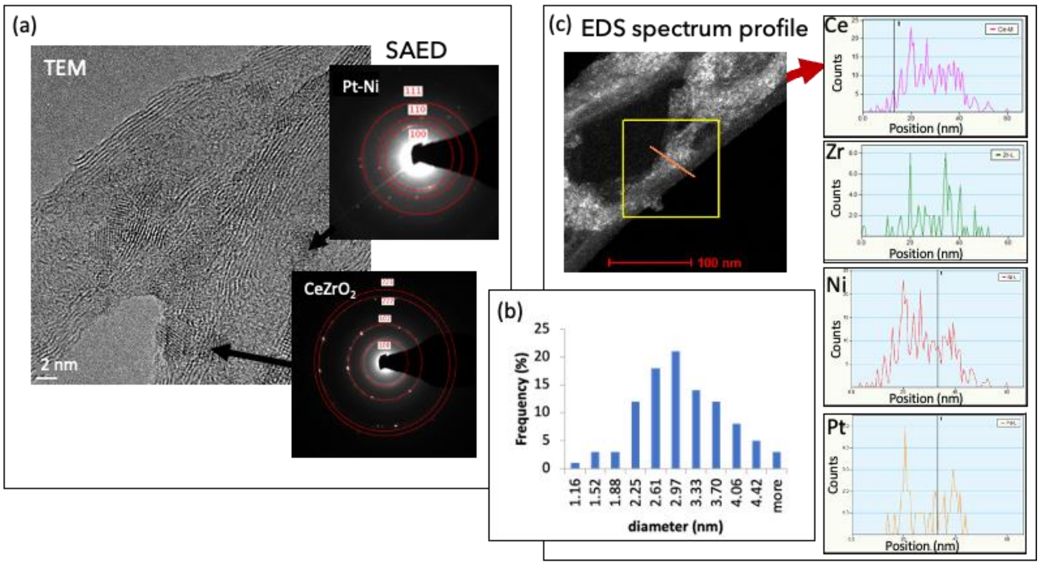

Figure 1. (a) TEM picture of the Pt-Ni-CeZrO$_2$/CNT with the SAED for Pt-Ni and CeZrO$_2$ nanocrystals. (b) The particle size distribution of the supported active phases. (c) EDS spectrum profile.

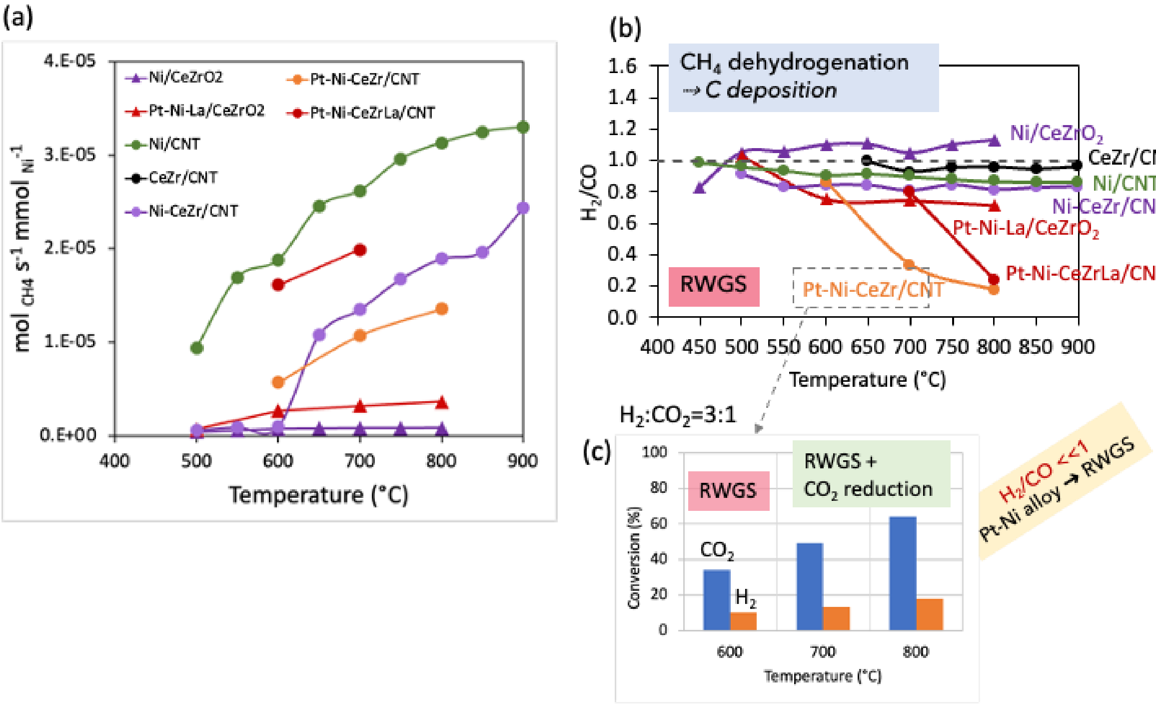

Figure 2. The performance of CNT and CeZrO$_2$ supported catalyst in DRM vs. temperature: (a) the rate of CH$_4$ conversion over calculated per Ni active site; (b) H$_2$/CO ratios. (c) the performance of Pt-Ni-CeZrO$_2$/CNT in RWGS reaction.

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Assessment of chlorine, sulphur and alkali compounds content in sewage sludge in terms of its thermal utilisation

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Keywords: sewage sludge, thermal utilisation, chlorine, sulphur, alkali metals

ABSTRACT

The amount of sewage sludge generated in Poland as well as in whole EU has remained more or less constant for several years [1, 2]. However, the utilization of sewage sludge is a serious challenge especially due to the reduction in the use of this waste in agriculture. Instead, thermal conversion is becoming increasingly prominent in sludge management. The proper execution of either incineration/combustion, co-incineration/co-combustion, gasification or pyrolysis of sewage sludge depends on a number of its physical and chemical properties. One of the crucial aspect for the thermal utilization is the content of contaminants such as chlorine, sulphur or alkali metals. These substances are responsible for, in particular, high temperature corrosion, slagging, fouling, formation of hydrogen chloride, dioxin, sulphur oxides and heavy metal evaporation [3, 4]. Due to the high variability of sludge properties and the legal regulations concerning the emission levels of pollutants from thermal utilization processes and the operating conditions, it is necessary to continuously monitor these parameters [5].

The research was carried out on samples of sewage sludge from various industries (food industry, refining, coking) and from a municipal wastewater treatment plant. Overall, 36 samples were analyzed. The total content of chlorine, sulphur and the basic composition of the ash (including the content of alkali metals), as well as the content of moisture and non-combustible matter were determined.

The chlorine content (on a air-dry basis) was in very wide ranges, from 0.04 to 3.21%, which was mainly due to the different sources of the samples. The total sulphur content of the samples also varied, from 0.57 to 5.98 % on a air-dry basis. The ashes obtained from ashing the analyzed samples at 550°C were characterized by a high content of total Na_2O+K_2O compared to conventional fuels and even biomass. The calculated Alkali Index also indicates that the analyzed sewage sludge can cause ash slagging and fouling in the installation.

The very high content of chlorine, sulphur and alkali in the tested sewage sludge especially sludge from wastewater from animal fat production and coke-ovens wastewater treatment plant can cause problems with the proper operation of the plant, thus forcing a control of the input composition or the operating parameters of the plant.

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Thermal and Hydraulic Calculations of the Finned Heat Exchanger, Taking into Account the Air-Side Nusselt Number on the Individual Tube Row

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Keywords: finned heat exchanger; Nusselt number; local heat transfer coefficient; CFD; air heat pump

ABSTRACT

Currently, when designing finned heat exchangers (FHE), the average value of the entire heat transfer coefficient (HTC) is considered. However, each row of the heat exchanger (HEX) has different hydraulic-thermal characteristics. The novelty of this research is to present the differentiation of the individual air-side Nusselt number in each row of FHE using CFD modelling. FHE has four-rows, circular tubes, and continuous fins with a staggered tube arrangement. Relationships for the Nusselt number derived for the entire exchanger based on CFD modelling were compared with those available in the literature, determined using experimental data. The maximum relative differences between the Nusselt number for a four-row FHE determined experimentally and by CFD modelling are in the range from 22% for a Reynolds number based on a tube outside diameter of 1000 to 30% for a Reynolds number of 13,000. The CFD modelling performed shows that in the range of Reynolds numbers based on hydraulic diameters from 150 to 1400, the Nusselt number for the first row in a four-row FHE is about 22% to 15% higher than the average Nusselt number for the entire exchanger. In the range of Reynolds number changes based on hydraulic diameter from 2800 to 6000, the Nusselt numbers on the first and second rows of tubes are close to each other. Correlations of Nusselt numbers derived for individual tube rows can be used in the design of plate-fin and tube heat exchangers used in equipment such as air-source heat pumps, automotive radiators, air-conditioning systems, and in air hot-liquid coolers. In particular, the correlations can be used to select the optimum number of tube rows in the exchanger.

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Electric car energy management strategy with an additional – Fuel Cell power module working in a continuous manner

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Keywords: electric car, fuel cell, methanol, reformer, operation

ABSTRACT

The issue of the operation of electric vehicles is closely related to the operational capabilities of the vehicle resulting from its intended use function and the possible range of the vehicle. Depending on the individual needs of the users, these two aspects alternate with the priority of each other. However, both of these features are closely related to the amount of energy available. Therefore, when we want to increase the amount of work performed by a vehicle, whether in terms of the functions performed or the distance covered, it is necessary to provide the right amount of energy on its board. Today, most electric vehicles store energy in the battery while charging when the vehicle is stationary. The amount of energy stored in the vehicle strictly depends on the capabilities of the battery. These possibilities depend on the type of chemical cells used in the battery and its electrical capacity. These parameters are generally constant, which consequently translates into a close dependence of the energy stored in the battery on the number of cells used and their operational state. Therefore, the operational capabilities of the vehicle directly depend on the size of the battery. The size of the battery is important in terms of vehicle design. The weight of the vehicle and the usable space as well as the cost of the vehicle depend on the size of the battery.

Taking the above into account, in the case of electric vehicles, the principles of individual selection of the power unit parameters should be introduced, strictly related to the potential user. Both in terms of his individual needs and on the basis of the characteristics of the time density of the energy demand of the vehicle used by him. These data can also be used to select the drive system of an electric vehicle additionally equipped with a power generation system using a continuously operating fuel cell. Continuous operation of the fuel cell as an element supplying electricity to the vehicle's energy system is highly recommended in terms of reducing the size of such a fuel cell and increasing its durability, which translates into a reduction in the operating costs of such a vehicle. Continuous operation of the fuel cell requires the provision of an appropriate amount of fuel, which is hydrogen. It is difficult to store in a vehicle, and therefore requires the use of appropriate tanks and protection, which currently significantly limits such installations in common use. Therefore, in the proposed solution, in order to ensure continuous operation of a small fuel cell, the fuel (hydrogen) will be obtained in the methanol reforming process, strictly according to the system needs.

The proposed solution requires a systemic connection of many operational processes, starting from the operation of the vehicle at a given moment, planned in the near future

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and in advance of several or even several dozen hours, both in terms of the vehicle load resulting from the number of passengers and the load resulting from the characteristics of the road traveled, weather conditions and the time of stops and the road situation resulting from other road factors.

All these factors should be included in the adaptive control algorithm of the power generation system to power an electric vehicle using a fuel cell powered by hydrogen produced for the operation of the cell in the methanol reformer located on board the vehicle in direct coupling with the fuel cell.

The test of such a coupling was carried out with the use of mathematical and physical models that approximate the individual components of the control model of the adaptive energy generation system. Modeling was performed using dedicated numerical tools. The article presents individual component models and conducts exemplary simulations to bring closer the undertaken research issues. The obtained results were verified against the initially adopted functional assumptions of the adaptive energy generation system for the continuous supply of an electric vehicle.

The works were carried out with the use of funds for the implementation of the project, co-financed by the National Center for Research and Development, under the "Smart Growth 2014-2020" Operational Program, the priority axis "Increasing the scientific and research potential", activities "Research and development work", sub-measure 4.1.4 "Projects application ". Own contribution, contractor-manager from the Poznań University of Technology. Contract number: POIR.04.01.04-00-0030 / 17-00 Project title: Adaptive control system for a hybrid electric energy generation system to drive an electric vehicle.

Classification of PCM Heat Exchangers for thermal energy storage

Moghtada Mobedi[1],*, ChunYang Wang[2]

Keywords: PCM heat exchangers, solid-liquid thermal energy storage, heat transfer

ABSTRACT

Many engineers and scientists attempt to find effective methods to use the renewable energy sources as well as utilize waste heat as a solution for energy problems. The unstable and/or transient behavior of renewable energy and waste heat sources force researchers to find solutions for energy storage. Solid-liquid thermal energy storage is one of options of thermal energy storage on which a large number of studies are done. It has advantages such as large amount of heat storage in a small temperature range.

PCM heat exchangers can receive heat from a fluid (or even a solid), store it and later it is released to another fluid (or a solid) whenever it is required. Its working principle is completely different than convectional heat exchangers since most of classical heat exchangers operate simultaneously meaning that the releasing of heat by one fluid and receiving of heat by another fluid occur at the same time. The classification of PCM heat exchanger is an important issue since it allows us to know the advantages and disadvantage of each type as well as to predict the application areas of each group. It helps us to have a systemically comparison between the PCM heat exchanger types which is an important issue for their improving. Information on the classification of conventional heat exchanger exists in literature and widely used in market [1]. However, to the best of our knowledge, there is only one study on the classification of PCM heat exchangers [2].

In this study, around 150 works were reviewed to classify PCM heat exchangers structurally. The result of this attempt for PCM classification showed that it is possible to classify PCM heat exchangers in three groups as a) working fluid embedded, b) PCM embedded, c) multi domains of working fluid and PCM. Each group can also be classified to the sub-groups. For instance PCM embedded type heat exchangers can be sub-grouped as a) shell and tube, b) triplex, c) cross flow and d) packed bed type PCM heat exchangers. The advantage and disadvantages of each group as well as their application areas are discussed. Number of studies on each group is obtained and compared with each other to discover the reason of interest.

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Energy storage in the era of Energy transformation. Can sodium batteries compete with lithium batteries?

Janina Molenda[1]

Keywords: Li-ion batteries, Na-ion batteries, electrochemical intercalation mechanism

ABSTRACT

Li-ion batteries are currently the most dynamically growing technology of electrical energy storage for mobile electronics, electric and hybrid vehicles, as well as for renewable energy storage and increased elasticity of large scale power plants. Lithium resources, however, are not sufficient for the constantly emerging new applications of Li-ion batteries. Therefore, the current world-wide efforts and interests are focused on exploring alternative technologies, one of which is Na-ion batteries. Sodium resources are abundant as this element is the fourth most common element on earth, leading to low cost of the raw material. Furthermore, a wide group of sodium compounds exhibit reversible reaction with sodium at a high voltage (3 – 4 V vs. Na/Na^+) and with high electrochemical capacity (200 mAh/g) enabling practical application in electrochemical energy storage with a similar mechanism of operation to that found in Li-ion batteries. Since nowadays cobalt and graphite are critical raw materials, so searching is focused on new cobalt-free and graphite-free electrode materials.

The author of this work basing on her own investigations of A_xMO_2 cathode materials (A=Li, Na; M=Ni, Co, Mn, Fe, Ti, Cu) has demonstrated that the electronic structure of these materials plays an important role in the electrochemical intercalation process [1]. The paper reveals correlation between crystal and electronic structure, chemical disorder, transport and electrochemical properties of layered Na_xCoO_{2-y} and $Na_xNi_{1/5}Co_{1/5}Fe_{1/5}Mn_{1/5}Ti_{1/5}O_2$ high entropy cathode materials and explains of apparently different character of the discharge/charge curve in those systems.

The battery on the base on the developed high entropy oxides $NaNi_{1/5}Co_{1/5}Fe_{1/5}Mn_{1/5}Ti_{1/5}O_2$ cathode materials are characterized by high potential, high capacity and high rate capability guaranteeing high energy and power densities. By using the structural analysis methods (operando XRD, XAS and Mossbauer spectroscopy) we described the mechanism that governs the sodium deintercalation/intercalation processes in $Na_xNi_{1/5}Co_{1/5}Fe_{1/5}Mn_{1/5}Ti_{1/5}O_2$ cathode with indicating the valence state of transition metals. Our investigation indicated that only titanium is electrochemically inactive during the cell operation, while Mn, Fe, Co, Ni undergo reduction and oxidation processes [2].

The detailed analysis presented in this work provides a strong proof that the high-entropy $Na_xNi_{1/5}Co_{1/5}Fe_{1/5}Mn_{1/5}Ti_{1/5}O_2$ oxide with reduced content of cobalt and nickel, might be applicable in sodium batteries technology, especially in terms of large-scale energy storage units.

Acknowledgements

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Properties of scandia and ytterbia doped zirconia examined by broadband impedance spectroscopy, XRD, SEM and XPS

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Keywords: Scandia-stabilised Yterbia-doped Zirconia, Solid oxide fuel cell, Broadband Electrochemical Impedance Spectroscopy

ABSTRACT

Solid oxide fuel cell (SOFC) is an electrochemical energy generator with the highest energy conversion efficiency. Cubic zirconia doped by trivalent yttria is the state of the art SOFC electrolyte. However, in the intermediate (500–700 °C) or low (350–500 °C) temperature ranges its ionic conductivity is too low. The more expensive scandia doped zirconia reveals enough high conductivity although it is not stable and undergo phase transition leading to less conducting tetragonal phase. Stable cubic phase can be obtained by doping zirconia by two cations. The goal of this work is to examine electrical and structural properties of $Yb_{0.12}Sc_{0.08}Zr_{0.8}O_{2-\delta}$.

The $Yb_{0.12}Sc_{0.08}Zr_{0.8}O_{2-\delta}$ powder synthesized using a sol-gel method was isostatically pressed in the pellet form and sintered at 1500 °C. The platinum ink was applied on both sides of pellet and sintered, then electrical properties were examined by broadband impedance spectroscopy. Structural, microstructural and electronic states of elements present on the surface were investigated by X-ray diffraction in the range 25–800 °C, scanning electron microscopy and X-ray photoelectron spectroscopy, respectively.

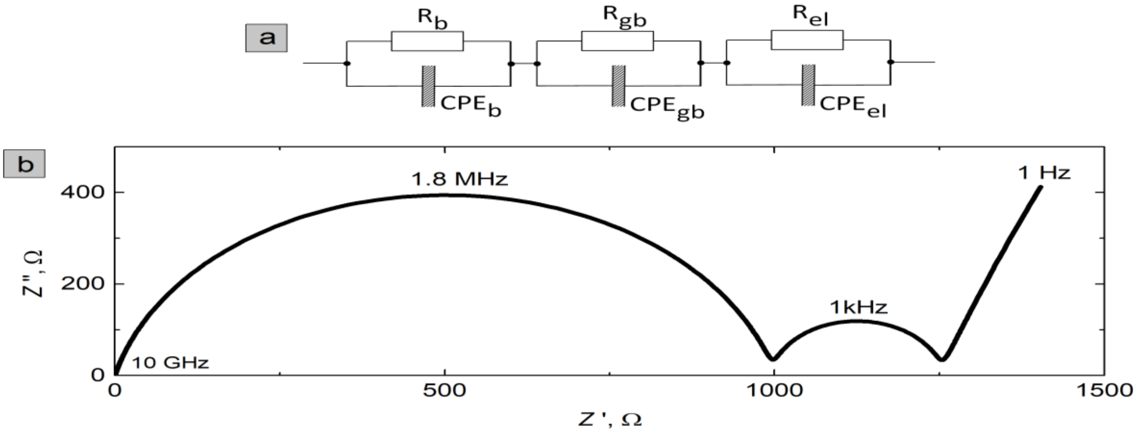

Figure 1. Equivalent circuit, which models ceramic conductor with electrodes (a) and simulated impedance spectrum of this equivalent circuit presented in complex plane (b).

The examined compound reveals stable cubic structure in the whole temperature

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range. The examined electrolyte exhibits high specific ionic conductivity with activation energies 1.06 and 1.15 eV of grain interior and grain boundary, respectively.

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Test benches and research work as a basis for determining the applicability of Turbine Pressure Stabilisation Systems for energy recovery and utilisation in a district heating network

Piotr Natkaniec [1]*, Piotr Dzierwa [2], Dariusz Borkowski [3]

Keywords: district heating, pressure stabilisation, turbine systems, energy recovery

ABSTRACT

The presentation aims to present the research work carried out to determine the relevance and feasibility of installing turbine installations whose task will be to stabilise the disposable pressure in the district heating network of the Municipal Thermal Energy Enterprise S.A. (MPEC S.A.) in Krakow while using recovered and transformed electrical energy. To this end, a key element became the creation of test stands operating in the actual conditions prevailing in the district heating network.

A key aspect in the process of designing the test stands, as well as determining their size and operating parameters, were the results of hydraulic calculations made using specialised software. The conceptual and design work carried out allowed the creation and preparation of test stands for analysing the operation of turbine systems. In addition, the work carried out resulted in the identification of optimum installation locations for both the test stands under consideration and potential target installations operating in the district heating system.

Testing will be carried out for two groups of equipment (installations). The basic criteria for this division are the power of the turbine systems and their application and the possibility of managing the recovered energy. Low-power installations will mostly be used in district heating chambers, where pressure stabilisation needs to be carried out, and the electricity generated by the turbine system will be used "on site" to power district heating infrastructure components, e.g. valve actuators, automation, lighting, etc. (OFF-GRID operation). On the other hand, systems with higher capacities will convert the recovered mechanical energy into electrical energy, which will be fed into the power grid via inverter systems (ON-GRID operation).

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NiMgAl mixed-oxides catalysts derived from hydrotalcites for efficient CO_2 methanation under both thermal and plasma conditions

Minh Nguyen-Quang[1,2,3]*, Federico Azzolina-Jury[1], Bogdan Samojeden[2], Monika Motak[2], Patrick Da Costa[3]

Keywords: DBD Plasma, CO_2 methanation, Hydrotalcite-derived catalyst, mixed-oxides.

ABSTRACT

Carbon dioxide is a major greenhouse gas mainly responsible for global issues, including global warming, an increase in a variety of disasters that impact both human and environmental aspects. Sabatier reaction (Eq. 1), also known as CO_2 methanation [1], has the potential to address these concerns in intergovernmental efforts where CO_2 can be recovered from waste gas sources and transformed into usable fuels and chemicals.

$$CO_2 + 4H_2 = CH_4 + 2H_2O,\ \Delta H^0_{298K} = -165\text{kJ/mol} \quad \text{(Eq. 1)}$$

It was regarded as one of the most advanced technologies for recycling CO_2 in the face of rising energy demands in the long run. CO_2, however, is a stable molecule that requires much energy to be activated (Eq. 1). In other contexts, plasma, particularly non-thermal plasma (NTP), when applied in combination with catalysts, enables for operation at moderate temperature and ambient pressure while still producing highly active species and electrons. In regard to CO_2 thermal and plasma catalysis, mixed-oxides derived from hydrotalcite [2] were chosen as parent materials in our study with further modifications in order to tailor the catalysts for this purpose.

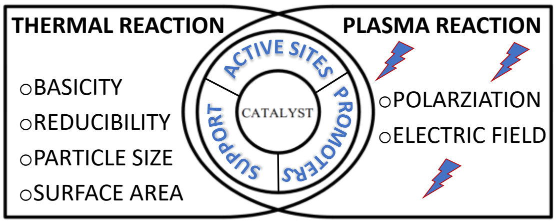

Fig. 1 Scheme of promotional effects of catalyst on thermal and plasma reactions

The results indicated that under thermal conditions, the parent NiMgAl-Hydrotalcite (NMA) showed a 78% CO_2 conversion and ca. 99.3% CH_4 selectivity at 300°C, at GHSV=12,000h^{-1}, whereas the catalyst after modifications with proper promoters (e.g. Fe, Co, Y, Gd) give 80-85% CO_2 conversion and 99.8% CH_4 selectivity at 250°C. Before modifying, NMA in a dielectric barrier discharge test showed an acceptable CO_2 conversion (nearly 65%) at 28W; the values were observed at a maximum of 86% of CO_2 conversion and nearly 100% CH_4 selectivity at 24W discharge power for promoted catalysts. Additionally, the maximum plasma temperature measured was around 190°C, with an energy density of 80%. These results proved that plasma-catalyst operating can surpass the reaction energy barrier more readily than thermal conditions. It was expected that a

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suitable promoter would enhance basicity, surface area, smaller particle size, and plasma features like promoting polarizability and altering electric field - in thermal and plasma conditions, respectively.

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Methanol production from carbon dioxide acquired from negative emission power plants using CFD approach

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Keywords: carbon capture utilization, Computational Fluid Dynamics, methanol production, kinetics of reaction, mass sources

ABSTRACT

Carbon dioxide is a significant environmental and economic issue in many industries. Its emissions continue to increase with the growth of industry, hence ways must be found to dispose of it. One solution is to build carbon capture power plants, which prevent CO_2 emissions to the environment while obtaining an additional manageable product [1,2].

Carbon dioxide has a wide range of applications, both in its pure form as an extractant in supercritical extraction or in natural gas extraction, but also as a substrate in many chemical reactions. One of the most important for energy reasons is the catalytic conversion of carbon dioxide to methanol, which can become an alternative fuel to hydrogen. Moreover, it is also used as a fuel additive or substrate for many subsequent syntheses, including polymers as well as plastics, and is also a very good solvent [3].

Methanol is a basic substrate for many industrial applications, so processes are being improved both in terms of process parameters, the substances involved in the reaction and the apparatus itself. Therefore, computer modelling techniques can help to understand the phenomena taking place in the reactors and also support the optimization of parameters [4].

In addition, developments in hydrogen production and carbon capture technologies are paving the way for a wider use of methanol in energy and transport. An example relating to carbon capture technology is the gas-fired power plant cycle with sewage sludge gasification and CO_2 capture, so as to minimize the human carbon footprint [5]. When integrating such a cycle using sewage sludge, we speak of Bioenergy with Carbon Capture and Storage (BECCS), while after using CO_2 for methanol production, the name Bioenergy with Carbon Capture and Utilization (BECCU) should be used [6]. The present study presents simulations of operation of a reactor for methanol production, which could become an integral part of the negative CO_2 gas power plant (nCO_2PP) cycle.

For this reason, this work focuses on the problem of Computational Fluid Dynamics (CFD) simulation of methanol production from carbon dioxide and hydrogen. As a numerical simulation software is still under development, an implementation of User Defined Function (UDF) into a commercial CFD tool was also undertaken, considering the theoretical and experimental dependencies of the kinetics of reactions under consideration. The main issue developed in this model is a proper selection of chemical equilibrium constants that enter indirectly into the production sources of the individual components. In the methanol production model, according to the literature [1,3,4], three main reactions are crucial. However, the rate of methanol production depends firstly on the choice of catalyst and secondly on the process parameters [7].

Based on the available literature, information on the models, reaction kinetics and parameters necessary to perform the CFD simulations was collected. This makes it possible to observe the concentration of the individual components during the process throughout the reactor (Figure 1).

As an example result, the mass fraction of methanol formed on the reaction surfaces of the catalyst is illustrated. It becomes apparent that with evenly checkerboarded wheels

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in the 2D flow, the concentration systematically increases, indicating the correct reactor geometry for methanol production. However, the degree of CO_2 conversion depends on the choice of catalyst and the research focus in this area is the discovery of new catalysts. Only a combination of experimental investigations, theoretical studies and numerical calculations can contribute to the design of highly efficient catalytic reactors.

It is worth mentioning that the results of the CFD calculations, once integrated in space, make it possible to obtain the parameters necessary for the analysis of thermodynamic cycles also directed towards CO_2 utilization.

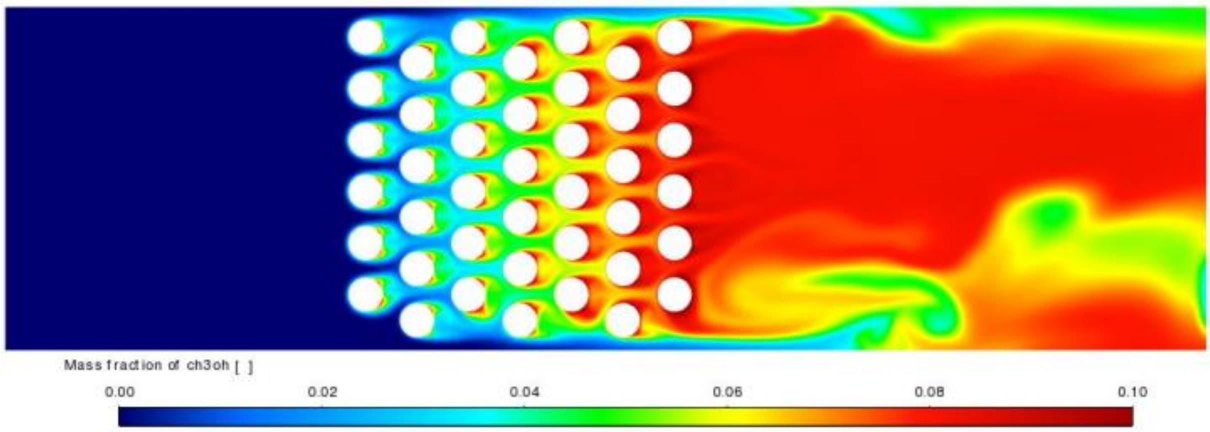

Figure 1. Mass fraction of methanol field in catalytic reactor

Acknowledgements

The research leading to these results has received funding from the Norway Grants 2014-2021 via the National Centre for Research and Development. This research has been prepared within the frame of the project: "Negative CO2 emission gas power plant" - NOR/POLNORCCS/NEGATIVE-CO2-PP/0009/2019-00 which is co-financed by programme "Applied research" under the Norwegian Financial Mechanisms 2014-2021 POLNOR CCS 2019 - Development of CO2 capture solutions integrated in power and industry processes.

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Secondary use of carbon filters used to purify water

Danuta Olszewska[1,*]

Keywords: adsorption, filters, catalysis

ABSTRACT

Nowadays, the reuse of materials is of great importance. We care about the environment. We care about health. Bottles with carbon water filters are in common use. The purpose of filters is to remove contaminants from drinking water. Thus, substances that may be useful in other processes are adsorbed on the filters. As you know, activated carbon can be a catalyst for many chemical reactions. And enriched with additional ions, it might work with better efficiency. The aim of the work is to demonstrate the chemical composition and physicochemical properties of used filters and to analyze the possibility of their use in catalytic processes related to the removal of pollutants from combustion processes.

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Selected Research Problems for Electrical Power Industry

Martin Ostoja-Starzewski[1]*

Keywords: helical electrical cables, dynamics, turbulent flow, shielding effectiveness

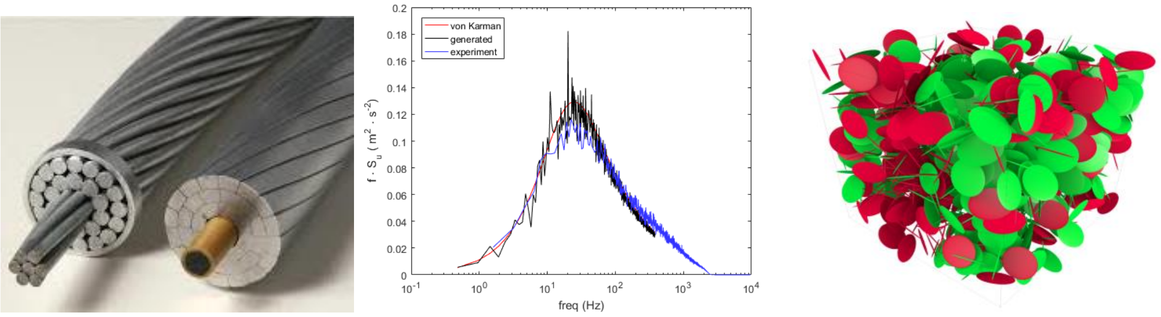
ABSTRACT

In this talk, we report several mechanics research problems studied within the NSF Industry/University Cooperative Research Center for Novel High Voltage/Temperature Materials and Structures at the University of Illinois. The overall objectives of our Center included (i) Design and development of novel and evaluation of existing HV energy transmission multifunctional materials for next-generation conductors, insulators, underground cables, and towers; and (ii) Design and development of novel advanced HT materials and evaluations of existing materials for aerospace, automotive, and other industrial applications. Following a brief overview of the structure and operation of our Center, we discuss:

Modeling of elastostatics, vibration, impact responses, heat conduction, and thermoelasticity in helically-wound cables [1-4], Fig. 1(a).

Statistical characterization of turbulent flows [5], Fig. 1(b).

Conductivity and shielding effectiveness of polymer nanocomposites [6-10], Fig. 1(c).



(a) (b) (c)

Figure 1. (a) Electrical conductor cables; (b) spectral densities in models of statistical turbulence; (c) a multicomponent nanocomposite.

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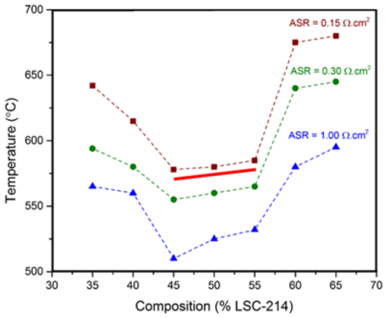
Development of Amorphous/Nanocrystalline LSC based cathodes for IT-SOFCs

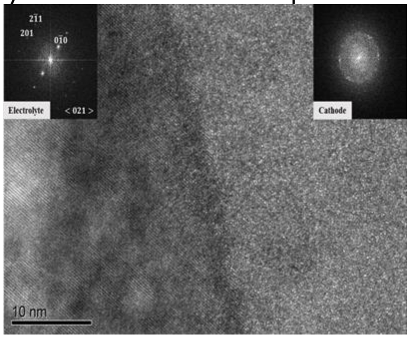
Tayfur Öztürk[1]

Keywords: ORR, Hetreo-interfaces, Symmetric Cells, Crystallization, Strontium Segragation

There is a considerable interest in the reduction of operating temperature of solid oxide fuels cell (SOFC). Thus, numerous studies have been conducted to develop the so-called intermediate temperature SOFCs. The bottle neck in IT-SOFCs is the cathode material as there are suitable alternatives for anode and electrolyte that could operate with acceptable kinetics at temperatures as low as 600 °C. In the case of cathode materials, the main problem is oxygen reduction reaction (ORR) which becomes unacceptably slow at reduced temperatures.



Temperatures at constant values of ASR as a function of cathode composition



TEM images of co-sputtered cathode and the electrolyte after annealing at 700 ⁰C for 10 days

In this study, a combinatorial approach was used to develop cathode materials with improved performance at temperatures in the range 500–700 °C. A thin film composite cathode library was obtained by co-sputtering of LSC-113 and LSC-214 onto suitably positioned substrates each with controlled compositions. The cathode library was screened with an electrochemical impedance spectroscopy using symmetric cells. The study showed that the compositions with volume fractions in the range 0.40 < LSC-214 < 0.60 is particularly significant in yielding cathodes of improved performance. Refocusing the combinatorial screening to this range yielded LSC-113:LSC-214=0.45:0.55 as the most favorable compositions. Taking ASR=0.15 Ω·cm2 as a useful benchmark, the study showed that cathodes in this range may be used at temperatures as low as 575 °C. It was further shown that composite cathodes have amorphous structures in co-sputtered conditions, and could remain so when used at reduced temperatures. At temperatures close to 700 °C the amorphous cathode turns into nanocrystalline two phase structure with grains not more than 10 nm in size.

The current work implies a new class of composite cathodes that are amorphous with enhanced ORR kinetics. They may be employed at the temperatures which are sufficiently low e.g. 575 ⁰C so that, aided by their inherent resistance to crystallization, they remain amorphous.

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Optimization of temperature distribution in steam reforming with radially structured catalyst

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Keywords: hydrogen, steam reforming, optimization, structured catalyst distribution

ABSTRACT

Introduction

The most recent rise of environmental awareness is currently inducing an emphasis on energy industry development. The energy producers are obliged either to reduce the emissions coming from conventional energy sources or even fully substitute fossil fuels with non-conventional sources. One of the proposed solutions is the application of hydrogen as an energy source. Unfortunately, the possibility of development for the hydrogen industry is limited. The most crucial issues regard scarcity of hydrogen and lack of proper distribution network. Regardless, new ideas for hydrogen exploitation are presented on a daily basis, indicating a perspective for the commercialization of the technology. The presented research regards the reaction of steam reforming, used for the production of hydrogen via conversion of hydrocarbons. Currently, steam reforming is widely used in industry, as a source of hydrogen for ammonia production. The character of the steam reforming reaction has a consequence in rather unfavorable conditions, influencing negatively both the process effectiveness and thermal degradation of the material used as the catalyst. One of the most crucial problems is the strong endothermic nature of the process. The rapid course of the steam reforming reaction leads to the creation of temperature gradients. The gradients lead to a non-uniform distribution across the whole reactor's volume. The non-uniform temperature distribution may result in a reduced lifespan of the catalyst and its uneven degradation, on account of occurring thermal stresses and rapid temperature changes. The presented investigation aims to limit the magnitude of the temperature gradients occurring inside the reforming unit. The macro-patterning concept is proposed to alleviate unfavorable thermal conditions. The proposed solution predicts the insertion of metallic foams. The catalytic insert is divided into separate segments, along the radial direction of the rector, resulting in five concentric cylinders, four of them hollow. The metallic foam segments are introduced to deliver superior thermal conducting properties when compared with the catalytic segments. The morphology of a specific segment may be altered independently, to allow for additional control of the reforming process course and products. The objective of the thesis is to verify the beneficial influence of macro-patterning introduction and define the optimal segments' compositi

Model

The calculations are conducted based on an in-house numerical code developed in the C++ programming language. The model is based on the fundamental transport equations and the steam reforming reaction kinetics. The optimization procedure is prepared by the implementation of a genetic algorithm and coupling it with the previously prepared numerical procedure used for the simulation of the reforming process and its conditions.

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Governing equations describing heat and mass transfer

$$\rho \nabla \cdot \mathbf{u} = 0,$$

$$\frac{\rho}{\varepsilon^2}\left(\mathbf{u}\cdot(\nabla \mathbf{u})\right) = -\nabla P + \frac{1}{\varepsilon}\nabla\cdot\left(\mu \nabla \mathbf{u}\right) - \frac{\mu}{K_p}\mathbf{u} - \frac{\rho c_{ine}}{\sqrt{K_p}}\mathbf{u}|\mathbf{u}|,$$

$$\rho C_p\left(\mathbf{u}\cdot(\nabla T)\right) = \nabla\cdot(\lambda \nabla T) + Q_j,$$

$$\rho\left(\mathbf{u}\cdot\left(\nabla Y_j\right)\right) = \rho\nabla\cdot\left(D_j \nabla Y_j\right) + S_j.$$

Chemical reactios dominant for steam reforming process

· methane/steam reforming reaction (MSR):

$$CH_4 + H_2O \Rightarrow 3H_2 + CO, \qquad \Delta H = 206.1 \left[\frac{kJ}{mol}\right],$$

· water-gas shift reaction (WGS):

$$CO + H_2O \Leftrightarrow H_2 + CO_2, \qquad \Delta H = -41.15 \left[\frac{kJ}{mol}\right].$$

Steam reforming reaction rate

$$R_{MSR} = \dot{w}_{cat} A_{MSR} \exp\left(-\frac{E_a}{RT}\right) p^{\alpha}_{CH_4} p^{\beta}_{H_2O}.$$

Equilibrium constant for water-gas-shift reaction

$$K_{WGS} = \frac{k^{+}_{WGS}}{k^{-}_{WGS}} = \frac{p_{CO_2} p_{H_2}}{p_{CO} p_{H_2O}} = \exp\left(-\frac{\Delta G^0_{WGS}}{RT}\right).$$

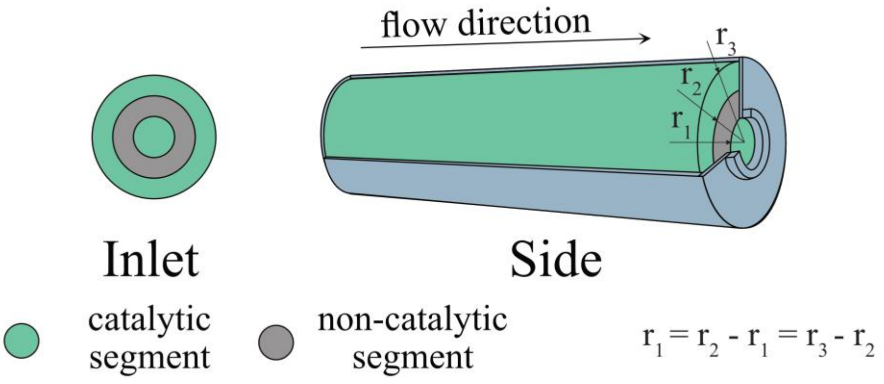


Fig. 1. Macro-patterned reactor geometry with catalytic insert divided in the radial direction

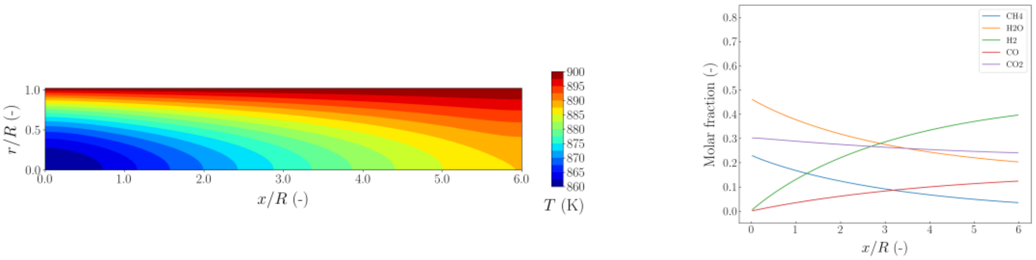
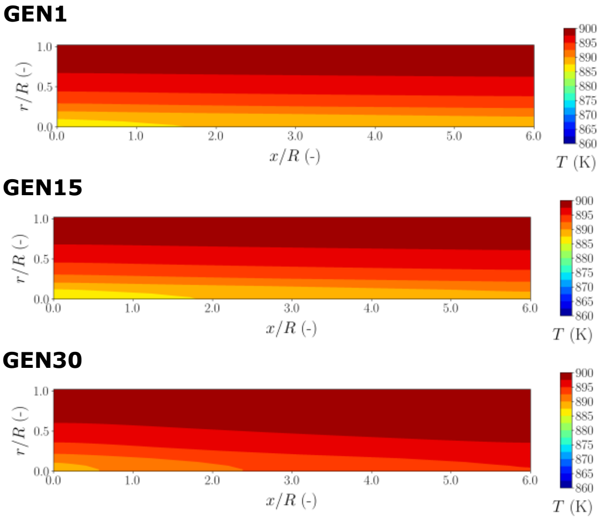
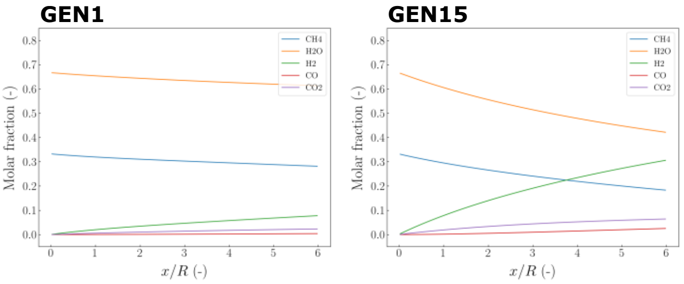
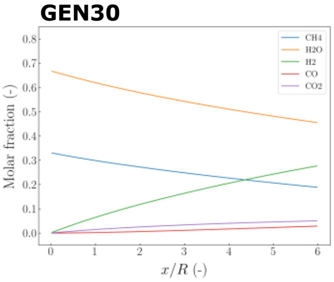


Fig. 2. Numerical results of reference case







Gen.	Fit (-)	CH4 Conv.	f_r
REF	0.543	0.783	0.271
1	0.430	0.152	0.840
15	0.464	0.212	0.841
30	0.605	0.426	0.874

Fig. 3. Numeral results of optimization procedure

The determination of chemical diffusion coefficient *D* and surface exchange constant *k* by the relaxation method

Norbert Raducki[1], Jakub Lach[1], Kun Zheng[1,2]*

Keywords: relaxation method, chemical diffusion coefficient *D*, surface exchange constant *k*, dimensionless parameter *L*

ABSTRACT

Among macroscopic methods applied for the determination of chemical diffusion coefficient *D* and surface exchange constant *k* of the mobile ions, relaxation techniques are widely employed, especially for the determination of these parameters in case of mixed ionic-electronic materials. In the practical studies, the mass or electrical conductivity variations are recorded during immediate changes of the oxygen partial pressure at elevated temperatures, to investigate *D* and *k* for mixed ionic-electronic conductors (for example in perovskite oxides) [1-4]. The theoretical basis for those relaxation techniques relies on a solution combining first and second Fick's law and flux density of the mobile species, through which the diffusion of mobile ions occurs [1, 2]. The respective solutions, depending on a geometry of the used sample, are different.

In this study, we discuss different theoretical solutions for the particular system (1-, 2- and 3- dimensional samples, sphere-shaped powder, etc.). The role of dimensionless parameter *L* for the determination of diffusion coefficient *D* and surface exchange coefficient *k* is systematically evaluated. The two-fold/single-fold diffusion behavior related with the proton and oxygen ion transport in proton conducting materials has been studied. The results showed that in materials with high values of *D* and *k* for proton transport and with a large difference of *D* and *k* between the coefficients of protons and the values of oxygen ions, the phenomenon of two-fold relaxation behavior is evident (see Figure 1). In addition, the porosity effect on the determination of chemical diffusion coefficient *D* and surface exchange constant *k* has been discussed.

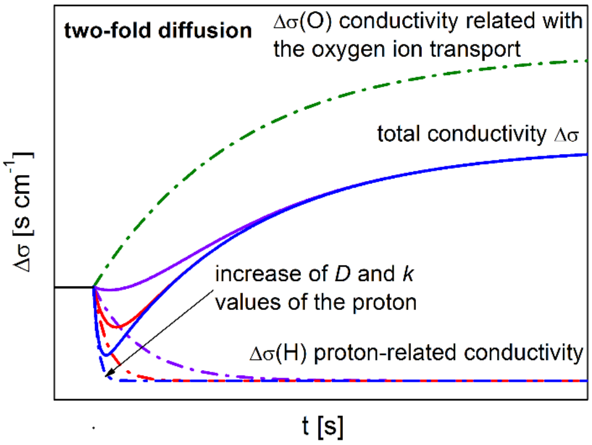


Figure 1: two-fold diffusion behavior in proton conducting materials.

Acknowledgment

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Renewable energy forecasting using deep neural networks trained by Rao algorithms

Venkata Rao Ravipudi[1]

Keywords: Renewable energy forecasting, deep neural networks, Rao algorithms

ABSTRACT

Recent research on forecasting renewable energy has become more important because of the growing interest in green energy. Traditional methods such as moving averages, exponential smoothing, autoregressive integrated moving average (ARIMA) models, etc. are used for forecasting. However, due to the inaccuracy of the conventional forecasting models, innovations in machine learning are needed to make an accurate forecast model that can be used in analyzing renewable energy sources to improve energy management services and the distribution of renewable energy sources. Solar irradiation forecasting will significantly impact the future of renewable energy. The National Aeronautics and Space Administeration (NASA) of the USA runs a project to collect renewable energy data worldwide including the solar irradiation data. The present study aims to build forecast models that use a deep learning technique to forecast the monthly solar irradiation in Surat city of Gujarat state of India based on the monthly data on solar irradiation obtained from the power project repository. In this work, we proposed a model that uses data related to monthly solar irradiation in Surat city and a deep neural network trained by the recently developed Rao algorithms for a more accurate prediction of future solar irradiation. Mean squared error and coefficient of determination (R^2) are used to compare how well the model fits and works compared to the ADAptive Moment (ADAM) estimation and Stochastic Gradient Descent (SGD) optimizers. The results indicate that the proposed approach of using deep neural networks trained by Rao algorithms can be effectively used for forecasting the monthly solar irradiance data. The same approach can be extended to forecast other renewable energy sources.

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The influence of charcoal addition to coking blend on bio-coke quality parameters

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Keywords: bio-coke, biomass, coke quality

ABSTRACT

Coke is an important raw material for the world economy. Along with iron ore, it is a key raw material in the integrated steelmaking process (BF-BOF), which currently accounts for over 70% of the world's steel production. Coke is also used, among others in the foundry industry, production of ferroalloys, insulating wool, quicklime, calcium carbide or as a fuel for heating purposes. The use of fossil based coke in these processes is associated with the emission of carbon dioxide, which is a greenhouse gas contributing to global warming. One way to reduce CO_2 emissions from coke production and from the processes in which coke is used (as a fuel or reducing agent) would be to replace fossil carbon with renewable biomass carbon, which is considered to be carbon neutral.

The aim of the presented study is to determine the effect of the addition of commercially available charcoal on the key quality indicators of the produced bio-coke. The tests were carried out for the conditions of the gravity (top) charged and stamp charged coke oven batteries. Charcoal was added up to 10% and the coke reactivity index CRI and strength after reaction CSR were assessed. The coking tests were carried out using the KARBOTEST large-scale laboratory installation (4 kg).

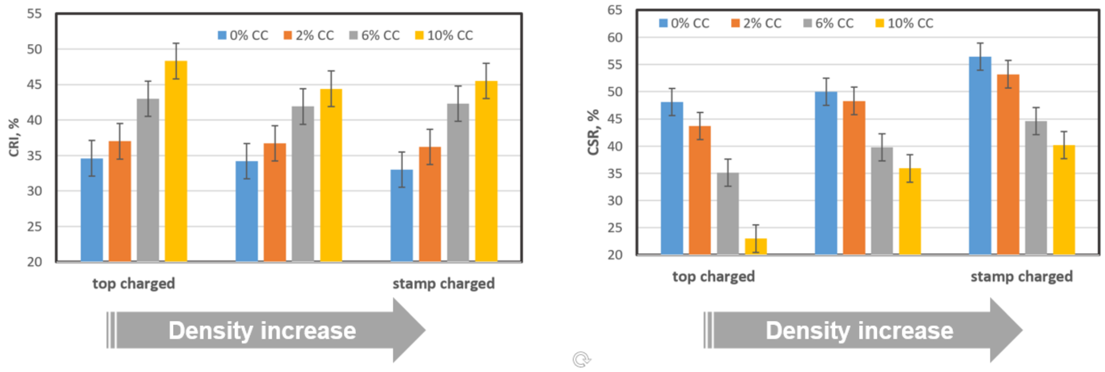

Figure 1. The CRI and CSR values of produced bio-coke

The addition of charcoal causes an increase in the CRI coke reactivity index and a decrease in the strength after reaction CSR. The deterioration of both parameters can be partially compensated by increasing the blend density (using a stamp-charging). The use of stamped charge allows to obtain bio-coke (6% charcoal) with a CSR similar to the CSR of coke obtained only from coal under the conditions of the gravity charging.

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Experimental determination of the fouling degree of a plate heat exchanger in a heat substation

Tomasz Romanowicz[1], Tomasz Sobota[2], Magdalena Jaremkiewicz[2,]*, Jan Taler[1]

Keywords: plate heat exchangers, thermal resistance of the deposits, Nusselt number correlation

ABSTRACT

The subject of the paper is experimental study on plate heat exchangers. The research concerns the determination of the degree of fouling of plate heat exchangers with mineral deposits contained in the water.

Plate heat exchangers are used in a wide range of industries. They are commonly used in heating, cooling, district heating as well as in various industries, e.g. food processing. Their popularity is due to the compactness of their construction and the high heat output in relation to their size. The overall heat transfer coefficient of plate heat exchangers is twice as high as that of shell and tube heat exchangers [1]. This is due to the embossing on the plates, which on the one hand disturb the flow of the medium between the plates, thus increasing the intensity of heat transfer, and on the other hand, stiffen the plates so that the heat exchangers can operate at high pressures. The disturbed fluid flow between the plates also makes it possible to partially flush out deposits from the exchangers (so-called self-cleaning), so they do not become fouled as quickly as shell-and-tube heat exchangers. The formation of deposits can also be reduced by using improved heat transfer surfaces through the use of a suitable shape or coating of plates [2-6] or by selecting an optimum fluid velocity [7, 8]. Despite this, deposits in heat exchangers must be removed regularly as they cause an increase in thermal resistance as well as an increase in fluid pressure drop due to a decrease in channel cross-section and an increase in fluid velocity. The fouling of plate heat exchangers by various types of deposits occurs regardless of the physical state of the medium [2, 3, 5] and can also be particularly acute in certain industries (e.g., the dairy industry [5]).

The method proposed in this paper for determining the thermal resistance of deposits is based on the determination of the overall heat transfer coefficient for a clean heat exchanger (operating under laboratory conditions) and a fouled one (operating in a heat substation). With the overall heat transfer coefficients determined, the difference in thermal resistance for the fouled and clean heat exchanger and thus the total thermal resistance of the deposits can be determined. The calculation algorithm presented in the paper will allow the creation of software that enables monitoring of the degree of heat exchanger fouling. The value of thermal resistance of the deposits determined online and pressure drops measured for each fluid, will be the basis for the decision to clean the heat exchanger.

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Metal-organic frameworks for CO_2 hydrogenation to methanol

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Keywords: metal-organic frameworks, MOFs, CO_2 conversion, methanol synthesis

ABSTRACT

Increasing concentration of carbon dioxide in the atmosphere has been considered a major factor contributing to environmental problems and progressing climate change. Thus, ideas or opportunities for its efficient transformation into more valuable chemicals and fuels have attracted noticeable interest from both academia and industry. In the recent years, industrial scale conversion of CO_2 was used to obtain products such as urea, formaldehyde, formic acid, or methanol, the latter being the most attractive and used as a fuel or a feedstock for production of chemicals [1]. However, because of exceptional thermodynamic stability of carbon dioxide particles, direct synthesis of methanol requires suitable catalyst, usually containing active copper phase. Industrially employed system – $Cu/ZnO/Al_2O_3$ was developed in 1966 and suffers from major drawbacks like low selectivity to MeOH and fast deactivation due to recrystallisation of Cu and ZnO, caused by water produced during reaction [2]. To prevent this, Cu phase might be immobilised inside of the metal-organic frameworks (MOFs), which can serve both as a support for active phase due to their excellent textural properties and as a catalytic promoter thanks to presence of easily accessible metal sites. Moreover, MOFs are susceptible to wide range of modifications which allow to adjust their properties and tailor their catalytic performance.

In this work, we report MOF-based catalysts for direct hydrogenation of CO_2 to methanol. The catalytic materials are UiO-66 structures modified by introduction of Cu with employment of double solvent impregnation method. In addition, the Cu/UiO-66 were obtained by crystallising MOFs around the already synthesised CuNPs. Prepared catalysts were described in terms of their chemical composition, crystallographic and textural properties, thermal stability, and morphology. Their catalytic performance was evaluated in the reaction of MeOH synthesis in a non-gradient, pressure reactor.

The research was financed by the National Science Center, grant no. 2019/35/D/ST5/03440 (PI: A. Łamacz).

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Impedance Spectra Analysis in Lead-Acid Batteries And Application Of Gerischer Element in Lead-Acid Battery Equivalent Circuits

Piotr Ryś[1],*, Maciej Siekierski[1], Piotr Biczel[2]

Keywords: Batteries, Lead-Acid, Impedance, State of Health, Diagnostics

ABSTRACT

In the recent years the field of battery diagnostics have seen increased interest from battery manufacturers, as well as, battery management system (BMS) designers. Various procedures to measure the State of Health (SoH) of a battery have been developed and implemented with varied degree of accuracy or success. For lead-acid battery, which are commonly used in uninterrupted power systems(UPS), a variety of procedures for the SoH assessment exist, but more methods have been considered to be used for battery diagnostics.

It was found that for lead-acid batteries the electrochemical impedance spectroscopy (EIS) can be used to assess the advancement of various ageing mechanisms occurring in them. This can be done by matching a correct equivalent circuit model to a lead battery and then analysing the EIS spectra to approximate the values of the circuit elements. And then by observing the changes in values of the model's elements, one can assess the battery's State of Health and advancement of any possible ageing processes. Currently a fair amount of research have been done to explore possible applications and integration of EIS into battery management systems. However, It was found during the course of research that the currently available equivalent circuits models for lead-acid batteries can be considered inaccurate.

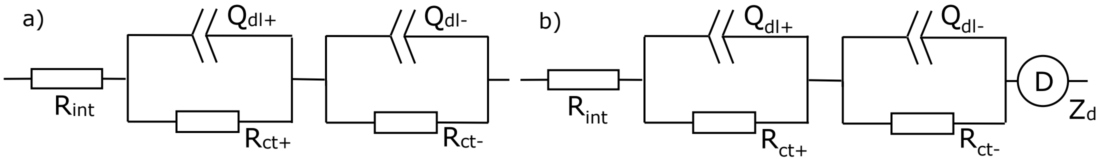

Figure 1. Equivalent circuit model of a lead-acid battery a) oversimplified b) with inclusion of a diffusion element

In the case of most papers and patents dealing with EIS application for SoH assessment in lead-acid batteries, it is proposed to use an equivalent circuit de from for the purpose of EIS spectra interpretation [1] (Fig. 1a). While for the higher frequencies (in the ranges of 2kHz to 50kHz) the model can be used to sufficiently describe the impedance spectra, for the frequencies below 2kHz it was found that this equivalent circuit is insufficient. The lack of a diffusion element causes a large degree of error for approximating the values of the model's elements. To mitigate that some lead-acid equivalent circuit models prefer to include a diffusion element Z_d in them [2] (Fig 1b). The most used diffusion element in these models is the Warburg impedance element, and in some cases a modified variant of it is used instead.

During the course of the research it was concluded the use of Gerischer element as the diffusion element of the equivalent circuit solved important problems of lead-acid battery modelling. The inclusion of the said element has also provided a better description

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of the diffusion processes that occur on the lead-acid battery electrodes [3]. The electrodes used in such batteries are often porous or have a porous-like surface. Furthermore, there are self-discharge reactions occurring on the electrodes. This makes the Gerischer element the best fit for describing diffusion in lead-acid batteries. Fits of the EIS spectra using the model using that diffusion element proved to be more accurate, especially in the low-frequency range in comparison to one using the Warburg element (Fig. 2).

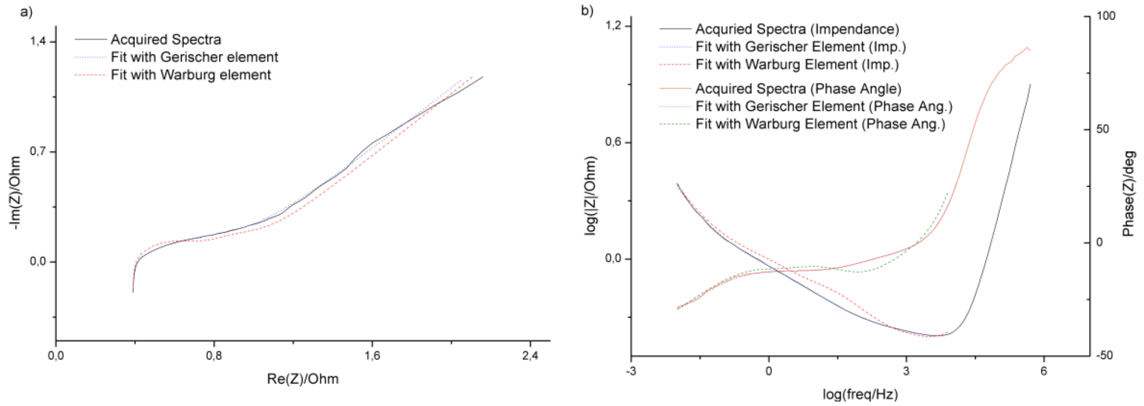

Figure 2. A Nyquist(a) and Bode(b) plots showing fitting of equivalent circuits that include a Warburg or Gerischer element in them.

It should be noted that in case of the impedance spectra being fitted with an incorrect model, one could assume that errors occurring in the low-frequency range (where the diffusion element exhibits itself in the spectra), should not affect the values of other elements. It is a false assumption, as application of incorrect equivalent circuit elements can affect the fitting functions output and in turn cause errors in other elements' values approximations.

It is worth noticing using this model, the values of the equivalent circuit elements can be approximated more accurately. For example in the case estimation of the battery's internal resistance (R_{Elec}) as seen in Tab.1 fitting the spectrum using the model with the Gerischer element approximates the values in a more interpretable manner for the purpose of SoC/SoH estimation.

Table 1. Values of R_{int} element at various states of charge

Element	100% SoC	75% SoC	50% SoC	25% SoC	0% SoC
$R_{int}[\Omega]$ (W) model	0.32	0.27	0.38	0.49	0.47
$R_{int}[\Omega]$ (G) model	0.28	0.31	0.33	0.42	0.44

In this particular example the data acquired from the fitting using the Gerischer element can then be used to produce a function describing relation between the internal resistance and battery's State of Charge.

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Technology of ultra-light composite hydrogen storage tanks for distributed energy systems

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Keywords: composite tank, type IV tank, hydrogen, distributed energy systems

ABSTRACT

Pressure tanks for compressed gases (including compressed hydrogen) are the most common engineering structures used in many industries. The current classification distinguishes tanks and cylinders in 5 generations. The project concerns the implementation of the production of Type IV tanks with an outer composite structure made of high-strength fiber and a hardenable resin and with an inner liner made of a thermoplastic polymer. Research assumes that the new composite tank will be intended for the automotive and aviation industries as well as mobile and fixed storage bundles.

Development and implementation of a breakthrough method of manufacturing fully composite storage tanks for compressed hydrogen are main goals of performed research. The main result of the work will be the development and production of type IV composite tanks with the following capacities: 1.2L, 6.8L, 120L, 195L for compressed hydrogen at a pressure of 35bar, 100bar, 300bar, 350bar, 700bar. Industrial research and experimental development works as well as pre-implementation works, including, among others, research on raw materials and development of methods for obtaining new material recipes and technological parameters for thermoplastic polymers with increased barrier properties, testing of internal liners of tanks, development of an innovative process of winding the fibers of the tank, as well as performing comprehensive permeability tests for hydrogen storage tanks in distributed energy systems.

The main research problems currently considered are:

- obtaining a sufficiently high tightness and barrier properties of the tank in relation to the stored hydrogen at high pressure.
- development and production of an appropriate braiding structure of filaments and a warp made of modified epoxy resin, allowing for compliance with the strength requirements of 700 bar standards.

As a result of the performed scientific research and implementation works, composite tanks will be characterized by, among others, the following functionalities:

- reduced weight of the tank,
- reduced weight of the inner liner,
- limited hydrogen permeability,
- purity of stored hydrogen,
- resistance of the tank wall to corrosion - no corrosion of type IV tanks
- safety of use,
- lower weight of storage bundles;
- longer service life of the tank compared to other types of cylinders,
- integrative functionality of composite hydrogen storage tanks in distributed energy systems.

The planned technical parameters of cylinder and implementation of the new technology presented above ultralight composite hydrogen storage tanks for distributed

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energy systems will allow for a significant competitive advantage in the global scope.

The performed research will contribute to promoting the use of hydrogen, which is becoming more popular in Europe as an alternative fuel and key energy carrier in energy transition. The use of hydrogen energy in propulsion systems is a pro-ecological alternative to petroleum-derived fuels, especially with use ultra-light composite tanks.

Application of modified vermiculites as catalysts in DeNOx

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Keywords: transition metals, vermiculite, DeNOx

ABSTRACT

The dynamic development of industrialized countries provokes contemporary society to take action to protect the environment. Currently, a number of studies are being carried out to reduce emissions of nitrogen oxides, which are considered extremely harmful to both human health and the natural environment. One of the methods is the reaction of selective catalytic reduction of nitrogen oxides with ammonia (SCR-NH_3). As the catalytic material, vermiculite modified with zirconia, cobalt, copper, iron and nickel.

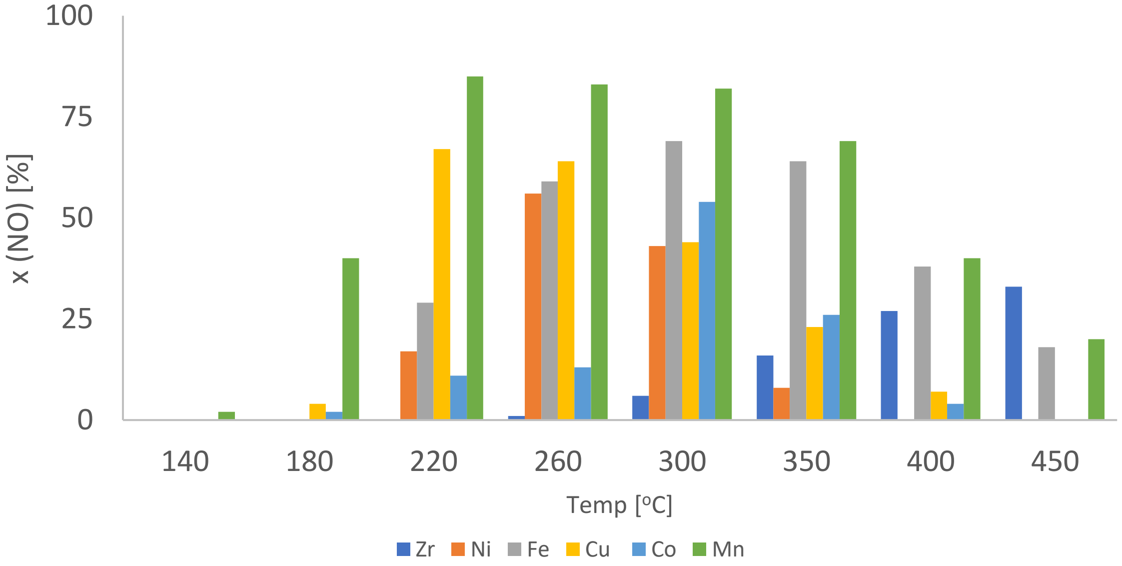

Fig. 1.NO conversion of studied catalysts. SCR conditions: 800 ppm NO, 800 ppm NH_3, 5% O_2,rest He, flow 100 ml/min, mass of cat. 200 mg

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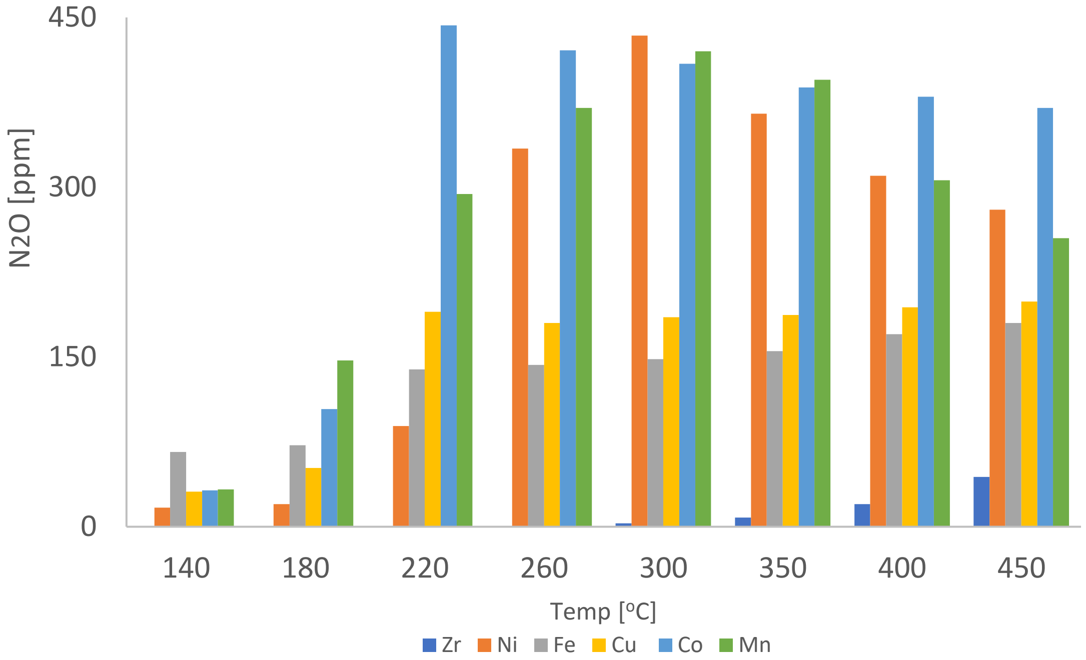

Fig. 2. N_2O formation of studied catalysts. SCR conditions: 800 ppm NO, 800 ppm NH_3, 5% O_2,rest He, flow 100 ml/min, mass of cat. 200 mg

In the case of applied manganese, iron and copper ions, satisfactory values of NO conversion were obtained, ranging from 65% to 90% at temperatures of 160-180 °C. However, despite the high degree of conversion, unfortunately, the formation of harmful N_2O was also found, which in the case of the catalyst with ions of cobalt, nickel and manganese was 400 - 500 ppm at temperatures of 180-260 °C.

Vermiculites modified with copper or iron showed the best catalytic properties in the SCR-NH_3 in low temperature range (<200 ^oC).

Acknowledgments: This work was supported by Grant AGH 16.16.210.476

Effect of potato starch and NaOH in the API filter of water-based drilling fluid in the oil industry

Juan C. Santivañez [1,*], **Walter Erick Cano** [1]

Keywords: Drilling fluids; Starch, PAC L; API filtering; Viscosity.

ABSTRACT

In this investigation, a drilling fluid (mud) system was formulated, to evaluate its API filtering, using Potato Starch as a filtering control agent; NaOH as a pH controlling agent, and bentonite as a viscosifying and densifying agent.

In this investigation, the effect of potato starch and NaOH on the water-based drilling fluid was evaluated with a mixed factorial design of 3*4*2, preparing 12 muds each in 1 bbl., with 28 lbs. of bentonite, (0,5; 1,0 and 1,5) lbs. of potato starch and (0,17; 0,27; 0,37 and 0,50) lbs. of NaOH which were tested for laboratory-scale API filtering under the ANSI API RECOMMENDED PRACTICE 13B-1 standard.

The tests that obtained that the Mud with quantities of potato starch (0,5 and 1,5 lbs.) and NaOH (0,27 and 0,50 lbs.) have the maximum and minimum values in the API filtrate (29,4 ml and 12 ml respectively). Potato starch is an economic and ecological substitute for PAC L as a filtering controlling agent. This generates an opportunity for the industrial development of potatoes in Peru.

Introduction:

Potato starch is a natural polymer, whose amylose/amylopectin ratio 20/80 respectively and phosphorus content makes it superior to products such as corn, cassava, and banana; This would indicate greater functionality as an additive for drilling muds.

The possibility of using potato starch as an additive for drilling muds could represent a reduction in costs since by presenting a higher yield than the products commonly used in the industry, a smaller amount of the product would be used thus reducing costs, this It would mainly benefit the companies that provide drilling services, since they can redirect the surplus budget to develop new technologies or new products that feed the process, thus allowing economic stability against the financial scenario.

Experimental design:

To determine the optimal drilling fluid conditions, a study was carried out based on the experimental matrix of a drilling fluid system. In this matrix, the concentration of potato starch and NaOH was varied, keeping constant concentrations of the other additives. In this case, the mathematical model has the following structure: 3*4*2, a factorial design with mixed levels. The matrix was tested for API filtering, Solids content, density, pH and rheology, to determine the appropriate concentration of potato starch and NaOH. The independent variables (amounts of potato starch and NaOH) were considered 3 levels for potato starch and 4 for NaOH.

All tests were carried out at an ambient temperature of 28 ° C (82.4 ° F) and an atmospheric pressure of 13.4 psi (0.912 atm). All these tests were performed under the standards established by the API (American Petroleum Institute) in the (ANSI / API RECOMMENDED PRACTICE 13B-1, 2017).

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Table 1. – Designation of each barrel[1] of formulated mud and its abbreviation. Source: self-made

Formulation	Composition (lb/bbl)			Denomination	Abbreviation
	Bentonite	**Potato Starch**	**NaOH**		
F. Standard[2]	**28**	**0.50[2]**	**0.50**	**Mud 0**	**M 0**
F. 1.1	**28**	**0.50**	**0.17**	**Mud 1**	**M 1**
F. 1.2	**28**	**0.50**	**0.27**	**Mud 2**	**M 2**
F. 1.3	**28**	**0.50**	**0.37**	**Mud 3**	**M 3**
F. 1.4	**28**	**0.50**	**0.50**	**Mud 4**	**M 4**
F. 2.1	**28**	**1.00**	**0.17**	**Mud 5**	**M 5**
F. 2.2	**28**	**1.00**	**0.27**	**Mud 6**	**M 6**
F. 2.3	**28**	**1.00**	**0.37**	**Mud 7**	**M 7**

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[1] All muds are designed using a barrel of oil as a reference with Pilot test design

[2] The standard formulation contains 0.5 lb / bbl of PAC-L

F. 2.4	**28**	**1.00**	**0.50**	**Mud 8**	**M 8**
F. 3.1	**28**	**1.50**	**0.17**	**Mud 9**	**M 9**
F. 3.2	**28**	**1.50**	**0.27**	**Mud 10**	**M 10**
F. 3.3	**28**	**1.50**	**0.37**	**Mud 11**	**M 11**
F. 3.4	**28**	**1.50**	**0.50**	**Mud 12**	**M 12**

Pilot test design requires calculating amounts of materials to put into the test samples for testing performed on proportionately small-scale samples. In pilot tests, a gram(g) is equivalent to pound(lb) and 350 cm3 is equivalent to one 42-gal oilfield barrel(bbl), or gram is equivalent to kilogram and 1000 cm3 is equivalent to one m3. In addition, one kg/m3 is equivalent to 2.85 lb/bbl.

Methods:

The experimental process of this research was carried out in the sludge and cement laboratory of the School of Petroleum Engineering of the Faculty of Physicochemical Engineering at the Industrial University of Santander - Colombia. The methodology we adopted for this research consisted of conducting the experimental tests of the potato starch and NaOH relationship in the mud to evaluate the API Filtering, to obtain the experimental data. With this data and parameter analysis, the relationship between potato starch and NaOH in its influence on the design of a water-based fluid was established.

Results:

It is observed that at a concentration of 0.5 lb of potato starch and 0.5 lb of NaOH a loss of filtration of 12 ml is obtained compared with a sludge prepared with PAC-L whose loss of filtration is 18 ml, The loss of filtering is less. Also, the values shown are similar to those obtained (Castro Cely, Gómez Cañón and Ariza León), which range between 6.0 and 11.7 ml for concentrations of 1 -4 lb/bbl of achira starch. The qualitative characteristics of consistency and elasticity describe excellent filter cakes for sludge whose composition contains 1.0 lb of potato starch and (0.27, 0.37 lb) of NaOH.

Conclusion:

The sludges formulated with the amounts of potato starch (1.0 and 1.5 lb) and NaOH (0.27 and 0.37 lb) have very stable values in the filtrate and within the filtering range with a minimum of 13 ml and a maximum of 18 ml in 30 min as required by the API filtering test. The use of potato starch improves filtering control, viscosity, and rheological properties (plastic viscosity, yield point, apparent viscosity, gel stress). Being potato starch is an economic and ecological substitute for PAC L as a filtering controlling agent, contributing to the preservation of the environment, reduction of operational costs and industrialization.

Table 2. - API filtration test Source: self-made

Mud	Consistency	Elasticity	Thickness of Filtrate cake (in)	Volume of Filtrate (ml)				
				7.5 (min)	15 (min)	20 (min)	25 (min)	30 (min)
M 1	Yes	Yes	> 1/32 "	20,0	23,0	24,5	26,0	27,5
M 2	Yes	Yes	> 1/32 "	8,0	11,0	11,5	13,0	14,5
M 3	Yes	Yes	> 1/32 "	14,0	17,0	18,5	20,0	21,5
M 4	Yes	Yes	> 1/32 "	7,0	9,0	10,5	11,0	12,0
M 5	Yes	Yes	1/32 ''	8,0	10,0	11,5	13,0	14,0
M 6	Yes	Very good	> 1/32 "	6,5	9,0	10,0	11,5	12,5
M 7	Yes	Yes	> 1/32 "	12,0	14,7	16,0	17,0	18,0
M 8	Yes	Yes	> 1/32 "	12,5	14,0	16,0	18,0	21,0
M 9	Yes	Yes	1/32 ''	13,4	15,0	17,0	19,3	22,4
M 10	Yes	Yes	> 1/32 "	19,0	22,0	25,0	27,0	29,4
M 11	Yes	Yes	> 1/32 "	7,5	10,0	11,3	12,3	13,3
M 12	Yes	Yes	> 1/32 "	6,0	7,5	8,0	8,5	9,7

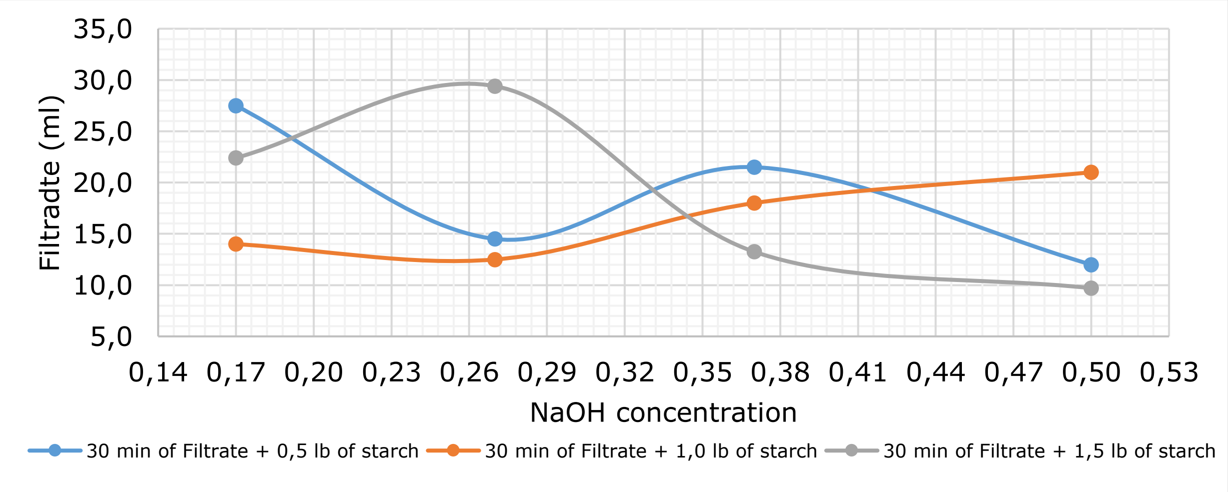

Figure 1. API filtering test (30 min.) Source: self-made

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Estimation of the electrical generation power of an ORC module using the geothermal potential of the production water of lot 95 operated by PetroTal in Peru

Juan C. Santivañez H.[1]

Keywords: Geothermal Energy, Production Water, Low-Enthalpy geothermal energy, Organic Rankine Cycle.

ABSTRACT

Introduction:

One of the problems in the oil fields with the water-drive production system is the amount of water that is produced. This situation is not unrelated to the oil fields located in the Marañón basin in Peru. These fields have production water cuts greater than 90%.

To date, PetroTal has implemented AICD technology in its wells to improve the productive performance of horizontally drilled wells by installing these valves at the subsurface level, thereby optimizing oil recovery during the useful life of the field. With the installed technology we still have a considerable water cut, in addition to its temperature, which we can consider high or low enthalpy in geothermal resources.

The closest projects, Block 192, and Block 8, present a water cut of 95 to 97%. It is also estimated that block 95 will reach a similar water cut. The main variables to manage in this type of reservoirs are the water flows and the surface facilities to be able to treat them and finally dispose of them as reinjection. The use of ORC modules for the generation of electricity from produced water, what we call cogeneration, is a new term in the oil & gas industry. Successful small-scale projects have been implemented using production flows from oil fields. An Organic Rankine Cycle (ORC) is a module consisting of 4 components: a heat exchanger, a turbine, a condenser, and a pump. The objective of this module is to take advantage of the thermal energy that comes from a geothermal fluid to generate electricity using a secondary fluid, such as propane, which has a lower boiling point than water.

To reach net-zero, PetroTal has seen fit to take advantage of the enthalpy of its production water, as well as its volumes, to implement an ORC module and thereby reduce its carbon footprint by a significant percentage in addition to co-producing. Electricity generation from geothermal sources presents more benefits compared to technologies such as solar or wind, due to the small area they cover to produce electricity compared to the other sources mentioned above, in addition to the availability of the resource, for geothermal projects it is 24 /7 and does not depend on any weather factor, only on the continuity of the geothermal fluid flow.

Methods:

To carry out the estimation of the electrical generation power of an ORC module using the geothermal potential of the production water of Block 95 operated by PetroTal in Peru, it is necessary to raise a series of considerations.

The estimates made by ORC module providers and another estimate using a rule of thumb with a study carried out for an oil field in Colombia using a simulation in HYSYS will be used to consider the other calculations on emissions of polluting gases and economic calculations to analyze its technical and economic feasibility of implementing an ORC

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Module in Block 95. which will provide us with the closest estimates of electrical generation power.

Results:

Estimates made by ORC module providers indicate that with current water flows (80 Mbbl/d) we can produce a minimum of 0.7 MWe and a maximum of 1.3 MWe. This generation power represents 16% of the current energy required by the field for its operation.

Provider	Scenario 1 MWe (with 80,000.00 bbl of water/d)	Scenario 1 (with 200,000.00 bbl of water/d)
Provider 1	0.7	-
Provider 2	0.85	-
Provider 3	1.2	5
Provider 4	0.73	1.5

Calculation of the effect of reducing CO2 emissions with the scenario provided by number 4

a) Preconditions
The capacity of the new generation plant: 0.7 MWe
Capacity factor: 85% 0.85
Time (hours/days): 8760

b) Calculation of the CO2 emission reduction effect
Crude oil consumption: 264.6 kg/MWh
Conversion to calorific value (TJ): 0.011277 TJ/MWh
Conversion to carbon exhaust gases: 0.226 T-c/MWh
Correction for the incomplete combustion portion: 0.223 t-C/MWh
Conversion to Carbon dioxide: 0.819 t-CO2/MWh

c) Annual energy production
Annual energy generation (MWh/year): 5212 MWh/year
d) Annual effect of reducing CO2 emissions
Annual emission reduction (kt-CO2/year): 4267.4 kt-CO2/year

Effect on the reduction of CO2 emissions
Therefore, when the geothermal power plant (0.7 MWe) has been completed, the CO2 emissions are expected to be reduced by 4267.4 Tons of CO2 per year.

And the calculation of the effect of reducing CO2 emissions with the scenario provided by number 3

d) Preconditions
The capacity of the new generation plant: 1 MWe
Capacity factor: 85% 0.85
Time (hours/days): 8760

e) Calculation of the CO2 emission reduction effect
Crude oil consumption: 264.6 kg/MWh
Conversion to calorific value (TJ): 0.011277 TJ/MWh
Conversion to carbon exhaust gases: 0.226 T-c/MWh
Correction for the incomplete combustion portion: 0.223 t-C/MWh
Conversion to Carbon dioxide: 0.819 t-CO2/MWh

f) Annual energy production
Annual energy generation (MWh/year): 7446 MWh/year
d) Annual effect of reducing CO2 emissions
Annual emission reduction (kt-CO2/year): 6096.3 kt-CO2/year

Effect on the reduction of CO2 emissions

Therefore, when the geothermal power plant (1 MWe) has been completed, the CO2 emissions are expected to be reduced by 6096.3 Tons of CO2 per year.

The project is economically viable over a 20-year horizon, including the sale of carbon bonds, at a unit cost of electricity production of $10/MWh.

NVP @ 10%, MM$	4
IRR %	30%
Pay Back, Years	4
ROI	0.86
LCOE ($/MWh)	14

Conclusions:

- From the estimation that the electrical generation power of an ORC module using the geothermal potential of produced water at flows of 80,000 bbl/d of water from block 95 operated by PetroTal in Peru is 1 MWe.
- This paper identifies the characteristics of the production water of block 95 operated by PetroTal in Peru are adequate due to the temperature and flow rates for the implementation of an ORC module.
- It is economically and technically feasible to implement an ORC module using production water from lot 95 operated by PetroTal in Peru. Over a 20-year horizon and at a unit cost of electricity production of $10/MWh

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NOx removal in a nitric acid plant by the SCR process

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Keywords: nitric acid plant, selective catalytic reduction, deNO$_x$, zeolites

ABSTRACT

The production of nitric acid is inextricably linked to the problem of atmospheric emissions of unabsorbed nitrogen oxides (NO$_x$) in the process. The concentration of NO$_x$ in the tail gases can reach more than 2,000 ppm. These are harmful gases that cause serious health problems and contribute to the formation of acid rain and photochemical smog.

Currently, the NO$_x$ emission limits set by the European Parliament Directive (IED) for new and existing nitric acid plants are set at 75 and 90 ppm, respectively [1].

The obligation imposed by the IED to reduce NO$_x$ emissions requires the use of effective methods to do it. Several NO$_x$ abatement methods can be used in nitric acid plants, such as high-efficiency absorption, non-selective catalytic reduction (NSCR), selective catalytic reduction (SCR), and absorption in sodium hydroxide solution [2]. The most effective and best studied is the widely used selective catalytic reduction of nitrogen oxides using ammonia as the reducing agent (SCR-NH$_3$).

Many types of catalysts are commercially used in the SCR-NH$_3$ process [3-5]. These are mainly catalysts based on transition metal oxides deposited on supports. The operating temperature range of these catalysts is typically 200-350°C. Within this "temperature window" these catalysts effectively reduce NO$_x$, but at higher temperatures, their activity and selectivity decrease by undesired oxidation of ammonia to NO or N$_2$O. In some plants, especially dual pressure plants, the tail gases temperature exceeds 350°C and even reaches 450°C. The most interesting alternative to commercial catalysts is catalysts based on natural zeolites. These materials occur abundantly in the environment and are relatively cheap, readily available, and active in the SCR-NH$_3$ process.

Łukasiewicz-INS, in cooperation with AGH, has developed a prototype zeolite-based catalyst [6]. The catalyst was prepared in the form of support pellets with an active phase, which is iron ions introduced into the zeolite structure by ion exchange from an iron(II) sulfate(VI) solution. The study showed that the iron-subsidized zeolite catalyst is active over a wide "temperature window." Laboratory tests of the catalyst's activity and selectivity were performed in the temperature range of 250-450°C, under real conditions, using tail gases from a pilot nitric acid plant. The effects of temperature and iron amount on catalyst activity in NO$_x$ reduction were studied. The most favorable composition was determined to achieve a NO$_x$ conversion rate above 90%, with no increase in the concentration of the by-product N$_2$O at temperature above 400°C. A catalyst with a suitable composition was selected and tested in the pilot plant under operating conditions similar to industrial conditions ($V= 12{,}3\ dm^3$, $GHSV= 11{,}000\ h^{-1}$, $T= 370\ °C$, $p= 4{,}3$ bar).

In addition, the activity of the commercial catalyst was measured under the same conditions in order to compare. The results showed that the developed catalyst has adequate catalytic properties, compared with the activity of commercially used catalyst.

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INTERNATIONAL CONFERENCE **ENERGY FUELS ENVIRONMENT EFE2022**
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Composites of phosphate-silicate proton-conducitve glass with uranyl hydroxy-phosphate and hydroxy-arsenate obtained by mechano-chemical synthesis

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Keywords: Medium temperature fuel cell, glassy protonic conductors, uranyl hydrogenphospahte/aresenate, composites, mechanochemistry

ABSTRACT

Introduction of hydrogen economy despite of its obvious technological problems arise a need of the significant number of the niche focused [1] solutions such as small sized (10-100 W) fuel cells able to run on hydrogen of lesser purity than this considered as a standard in the case of PEMFC's. One of the solutions can be derived from the fact that the increase of the operational temperature of the cell significantly decrease its susceptibility towards the catalyst poisoning. Electrolytes suitable for the so-called medium temperature operational range (120-400 °C) [2], hence developed [3,4], are neither commercialized nor standardized [5]. Amongst them phosphate silicate proton-conductive glasses were found not only to reveal interestingly high levels of operational parameters, but as well, to exhibit superior chemical and electrochemical stability over their polymeric counterparts.

On the other hand several drawbacks of these materials including lesser mechanical stability against cracking and still unacceptable fragility against high temperature dehydration encourages for further elaboration of the systems of interest by means of both improvement of the synthetic schemes, as well as, preparation of novel multi-component composite materials. Experimental routes available include here not only dispersing of the solid filler in the sol, co-precipitation, but as well as, processes such as mechanochemistry. The latter approach bases on the idea of application of mechanical phenomena delivering energy into the system of interest to induce the chemical reaction occurring in solid state. In our previous research we have proved that mechano-chemical approach to the formation of composites based on the amorphous phosphate-silicate glass based matrix severely change the properties of the dispersed crystalline phase ($CsHSO_4$) leading to the phase transition. Upon delivery of the mechanical energy the original material was not converted from the low temperature monoclinic structure – phase I into the intermediate temperature monoclinic structure - phase II. Moreover, the latter structure is found to be stabilized in ambient temperatures range.

In our current work composites of phosphate silicate glass obtained by means of in-house modified sol-gel approach with crystalline protonic conductors from uranyl hydroxy-phosphate and hydroxy-arsenate family were formed my means of mechano-chemical process occurring in a high-energy planetary mill. First of all it is worth noticing that all the results presented clearly prove the assumption that the mechanochemical treatment of the materials studied affects their properties even when pristine components are considered. In the case of pure phosphate silicate glass an order of magnitude higher values of the conductivity were determined for the milled-pressed material in medium temperature range (100-130 °C) (see Figure 1) when compared to the reference monolithic specimen of the amorphous material characterized with the same chemical composition and preparation procedure. On the hand the

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treatment involved leads to an order of magnitude increase of the respective activation energy what stays in contradiction to the general rule of thumb describing the charge transport properties of ionic conductors. In consequence the room temperature conductivity of the powdered material is significantly lower when compared with the one exhibited by its initial form. Moreover, a significant but differing in nature deviations are observed for both pristine crystalline materials upon milling. They reveal opposite changes in their properties including decrease of their conductivity, as well as, an about twofold decrease of the respective activation energies. In addition to that an about 30 °C increase of the temperatures of the structural transition specific to them is observed.

A similar conclusion can be, as well, derived for all the composites studied. In this case the nature of the observed changes strongly depends on the composition of the materials investigated. While low (10 to 20 w/w%) contents of both crystalline additives results in systems of limited stability, and therefore, inferior properties an opposite situation can be observed if higher (44 to 82 w/w%) amounts of the uranyl based compounds are considered. It was, thus, found that phosphate based compounds exhibit properties superior when compared with their arsenate based siblings.

Finally, the protonic transport mechanisms related investigations were performed for two composite samples K1 (44 w/w% of HUP) and K4 (82 w/w% of HUAs). First of all investigation confirmed a purely ionic character of conductivity with no electronic contribution what was expected upon the chemical composition of the material. More valuable are results proving the predominantly proton-related charge transport occurring in both materials. The values determined span between 0,945 and 0,982 depending on both temperature and sample composition. First of all it clearly observable that both t+ values monotonically increase with temperature (see Figure 2 for details). In consequence, a small but clearly observable and stable deviation (Δt+ =~0,01) of the determined values can be found between two materials tested with lower values characterizing the one containing higher amount of HUAs component.

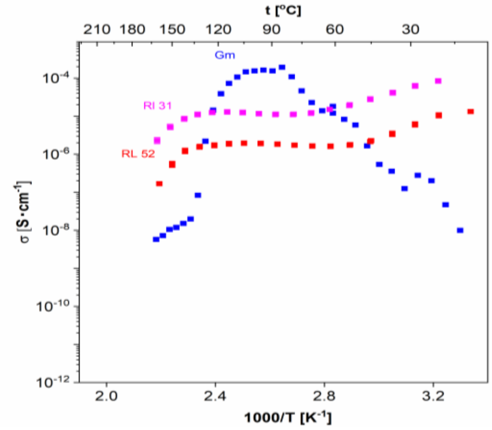
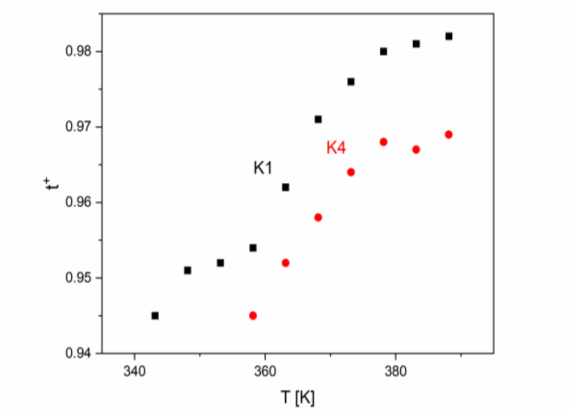


Figure 1. Comparison of the temperature dependencies of ionic conductivity of monolithic PSG and pelletized pulverized material of the same composition.



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Source apportionment of carbonaceus particulate matter (PM_1 and PM_{10}) collected in Kraków based on the carbon isotope analyses

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Keywords: particulate matter, carbon isotopes, air pollution

ABSTRACT

Krakow (Poland) is the second largest city in the country with the population of almost 1 million inhabitants. The city has been struggling with the problem of air pollution for years. During the heating period (autumn-winter), the permissible standards for particulate matter concentrations were regularly exceeded. Consequently, the Krakow City Council introduced a total ban on combustion of solid fuels starting from September 1, 2019.

Presence of carbonaceus fraction of suspended particulate matter in urban areas is mainly related to anthropogenic activity. These include, for example, the combustion of fossil fuels for heating purposes and emissions from transport. However, biogenic sources, including biomass combustion and plant pollen released into the air are also considered as a part of the carbon reservoir.

We report here the results of isotope analyses of carbon fraction of air particulate matter (PM_{10}, PM_1) from one-year campaign conducted in Krakow from April 2018 to March 2019 (the period before implementation of the above-mentioned ban).

In order to analyze the ^{13}C content in the carbon fraction of the analyzed samples, the isotope ratio mass spectrometry (IRMS) analysis was performed on a Finnigan Delta-S mass spectrometer. The measured $\delta^{13}C$ values ranged from -26.1‰ (April 2018) to -24.2‰ (December 2018) for the PM_1 fraction and from -25.5‰ (October 2018) to -24.2‰ (February 2019)) for the PM_{10} fraction. In addition, the radiocarbon concentration was analysed with the aid of Accelerator Mass Spectrometry (AMS). The measured ^{14}C content in the aggregated monthly samples, expressed in pMC (*percent modern carbon*), ranged from 37.8% (December 2018) to 57.9% (July 2018) for the PM_{10} fraction, and from 46.5% (December 2018) to 62.4% (April 2018) for the PM_1 fraction. As expected, lower levels of radiocarbon were recorded in autumn and winter months, while higher pMC values were measured during spring and summer. This indicates that increased emissions of carbonaceous particulate matter to the Krakow atmosphere is mainly caused by the combustion of coal in the city during heating season (coal is devoid of radiocarbon).

The measured $\delta^{13}C$ and pMC values obtained for carbonaceus fraction of the analysed PM_{10} and PM_1 samples were used in the emission source apportionment of this fraction for different seasons of the year in Krakow, based on the isotope-mass balance approach.

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Green hydrogen production in co-gasification of biowaste and sewage sludge

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Keywords: clean technologies; waste utylization; hydrogen; CO_2 capture

ABSTRACT

The global energy demand, degradation of the natural environment and the rising threat to energy security make the need to search for new environmentally friendly energy technologies still valid [1]. Nowadays approximately 70-80% of the world electricity is generated from fossil fuels [2]. Moreover, 80% of anthropogenic CO2 emissions originate from the combustion of conventional fuels [3]. However, the clean, environmentally neutral and generated in a cost-effective way energy carrier, hydrogen, seems to be a future solution to all these challenges. Hydrogen it is differentiated by a colour denoting how clean its production process is as grey, blue and green hydrogen [4-6]. The grey hydrogen is produced from fossil fuels (mainly in the process of steam reforming of methane (SRM), and coal gasification), the blue hydrogen is produced in steam reforming of methane combined with CCS), whereas the most desired green hydrogen is produced from renewable sources (via water electrolysis as well as thermochemical conversion of biomass and biowaste) [5,7,8].

In the paper the results of the systematic study of oxygen/steam co-gasification of biowaste blends with sewage sludge are presented. The co-gasification experiments were conducted in a lab-scale installation for thermochemical conversion of solid fuels in the process of pyrolysis, combustion or gasification. The experimental campaign covered series of tests at temperatures of 700, 800 and 900°C, respectively. Moreover, a comprehensive analysis of the experimental results of co-gasification and the physical-and chemical parameters important for the co-gasification process performance were conducted with the application of a chemometric method.

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Process of obtaining diesel substitute through plastic pyrolysis using hydrogen from coke oven gas - material and energy balance

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Keywords: plastic pyrolysis, diesel substitute, coke oven gas, hydrogenation, waste-derived fuel

ABSTRACT

According to a report by the Główny Urząd Statystyczny [1], 12.8 million tons of municipal waste were generated in Poland in 2019, of which only 25% were recycled, and a majority of waste (43%) were sent to landfills. The use of plastics in everyday life is becoming increasingly popular. They have become a dominant material in many areas of life, such as the packaging industry. Plastics are one of the most interesting fractions found in waste. Once plastics are separated from the waste stream, they can be recycled or thermally transformed.

One method of thermal processing of plastics is pyrolysis. This process yields char, pyrolysis oil, and pyrolysis gas. Char obtained by pyrolysis can be used in the production of sorbents, and pyrolytic gas is most often consumed to provide energy for further pyrolysis, making the process completely autothermic. The most interesting product seems to be the pyrolytic oil, which has properties similar to diesel fuel [2]. After appropriate benefication of this oil (e.g., undergoing a hydrogenation process), a component can be obtained that can be successfully blended with standard diesel fuel, thus reducing its consumption.

The choice of pyrolytic processing of plastics can be supported as follows:

1. Plastics production is increasing dramatically worldwide and when these products are out of use, they become waste going to landfills or become scattered waste, causing serious environmental and health problems.
2. Plastics biogedrate, photograde and oxidize very slowly, and when this process occurs, microplastics or substances such as toluene, benzene, phenols, or xylenes are released into the atmosphere, soil, and water, which are extremely toxic and pollute the environment.
3. Recycling is only a temporary solution because after a few cycles the plastic is not suitable for further processing. In addition, recycling is a very labor-intensive process, and its costs are high, as is the loss of material during the process. Also, recycled products are often more expensive than products made of new plastic and may not have the original properties.
4. From a sustainability point of view, the conversion of plastic waste to fuels or individual monomers leads to much greener waste management than the storage of it in landfills.
5. The quality of the oil produced from plastic pyrolysis is comparable to that of conventional diesel fuel (combustion heat of 45 MJ/kg, no sulfur, low water and ash content, almost neutral pH)

A promising direction for hydrogen production is its separation from coke oven gas. As a result of the coal coking process, a variety of products are obtained, such as: coke, coal tar, or coke oven gas. The typical composition of the coke oven gas is as follows: hydrogen (about 55%), methane (23-27%), carbon monoxide (9-10%), nitrogen (about

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5%), heavy hydrocarbons (about 3%), carbon dioxide (about 3%), oxygen (about 0.5%).

The gas is particularly rich in hydrogen and methane. About half of the gas obtained is diverted to fuel the coke oven battery. The remainder can be used for a variety of purposes, and its use depends mainly on the technology of a particular coking plant. Taking advantage of the fact that this gas is particularly rich in hydrogen, an attempt can be made to separate it and use it in other industrial sectors.

The diesel substitute production scheme is shown in Figure 1.

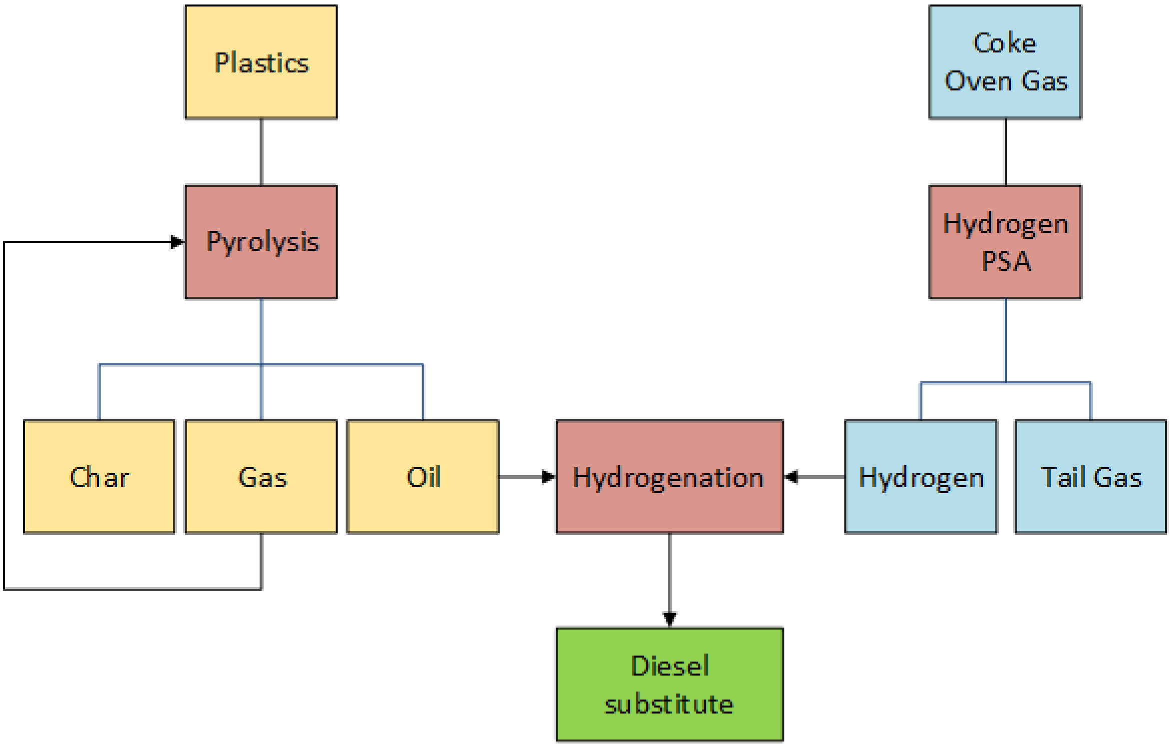

Figure 1. Diagram of the balanced system

As a result of the calculations, the material and energy balance of the entire process, as well as the individual stages, was obtained. From 1000 kg of plastics, approximately 545.85 kg of diesel component with a calorific value of 43.5 MJ/kg can be produced, consuming 27.67 kg of hydrogen. The by-products are: char (120 kg), and tail gas (384 m^3) with a calorific value of about 24 MJ/m^3.

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Determination of monohydroxylated metabolites of PAHs in wastewater

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Keywords: Hydroxy derivatives of polycyclic aromatic hydrocarbons, biomarker, wastewater

ABSTRACT

PAHs are common environmental pollutants resulting from incomplete combustion of organic materials. PAHs have been the subject of increased attention in air pollution studies for many years, as some of these compounds have been found to be carcinogenic or mutagenic. Most of the high molecular weight PAHs only degrade slowly and therefore pose a long-term potential risk to health and the environment. Therefore, it is important to assess the exposure of PAHs, especially in urban areas. Exposure to PAHs causes a number of negative health effects, including: reproductive defects, DNA mutations, leukemia and cancer of the lung, bladder, bone, brain and scrotum. Once PAH enter the human body, they are fairly rapidly metabolized and leave the body within a few days, primarily through excretion in the faeces and urine.

The aim of the study was the analysis of selected biomarkers (1- and 2-hydroxynaphthalene, 2- and 9-hydroxyfluorene, 9-hydroxyphenenthrene, 1-hydroxypyrene and 3-hydroxybenzo(a)pyrene) in wastewater treatment plant (WWTP), to identify the profile of metabolites as well their level of concentration in influent and effluent. Wastewater samples of the major WWTP in Krakow were collected in August 2020 and January 2021. Solid phase extraction (SPE) was used for the extraction of hydroxy derivatives of polycyclic aromatic hydrocarbons from the aqueous phase. Analyses of samples after derivatization with N-tert-butyldimethylsilyl-N-methyltrifluoroacetamide were carried out with the usage of GC-MS/MS.

Average concentrations of compounds were from 5 ng/L to over 400 ng/L. The highest concentrations of OH-PAHs were detected in the influents, for 2-OH-NAP and 9-OH-FLU in winter as well as in summer. However, their concentrations were 2 times lower in summer. The similar trend was observed for other compounds. 1-OH-PYR were observed for influent and effluent samples only in winter at average concentrations 8 ng/L and 5 ng/L, respectively.

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Effective using of renewable energy sources

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Keywords: energy auditing, BMS, renewable energy sources, energy efficiency

ABSTRACT

Using renewable energy sources in modern or renovated buildings is a must, if the building should meet the requirements of the directive [1] of nearly zero energy buildings. Rapid increase of the prices of fossil fuels in recent years causes that reduction of the energy demand became for many householders as a matter of their financial stability. The problem is significant for the whole of Europe because according to the European Commission [2] 51% of the energy used in Europe covers for heating and cooling demands of the buildings. Renewable energy sources covered only 14% of the energy demand of the buildings in the EU in 2012. All the rest is produced from fossil fuels [2].

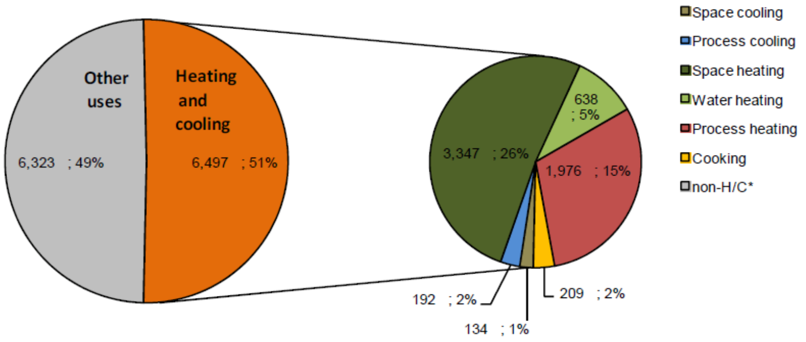

Figure 1 Final energy demand for EU28 by end-use for H/C in all sectors in 2012 [TWh] [2]

To maximize the results of RES use it is necessary to use controllers with proper programs. If more than one renewable energy source is used it is not enough to use a controller granted by the producer of a heat pump or solar collector system. The external building management system is necessary to control a few energy sources. Main features of such system are:

1. Using the energy in an efficient way in the building. The comfort temperature for inhabitants should be granted, but the house should not be overheated. So the program should measure the temperature outside or in more sophisticated systems use also the weather forecast.
2. Using RES should be a priority, boilers for fossil fuels should be used as the last step, if the energy cannot be supplied form RES. We have sunlight during the day, when the outside temperature reaches the highest level during the day. So using systems based on sunlight energy must be connected with using an energy bank. The storage capacity of such an energy buffer is always limited. For more effective use of such buffers it is necessary to control load and reload it from different energy sources.

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3. If there is more than one renewable energy source it is necessary to control all of them, giving priority to the system which at the moment is the most effective one.

The article shows the examples of such systems in a single family building and bigger one used by many inhabitants.

Single family house located in the southern part of Poland was originally equipped with a gas boiler only. The heating space is 180m2.

During the renovation of the building following changes have been done:

1. Windows were replaced with new ounces of $U<0,9\ [W/(m^2 \cdot K)]$
2. Doors were replaced with new ounces of $U<1,1\ [W/(m^2 \cdot K)]$
3. Heat pump was installed
4. Photovoltaics 19kWp and electric boiler were introduced
5. Exhaust fumes heat exchanger reducing the chimney loss at the gas boiler.

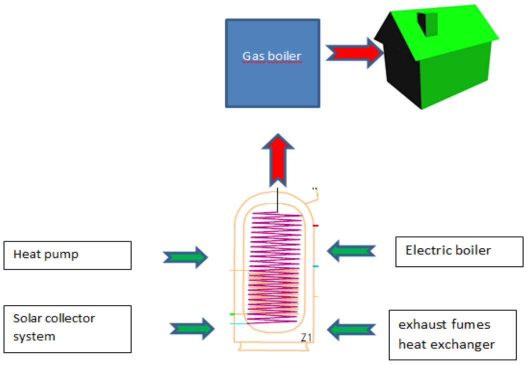

Figure 2 Energy recovery diagram (source: Tomasz Sumera)

By proper controlling the diverse Res system the 62% reduction of natural gas quantity was reached.

The second example descripted in the article is a Monastic house which has also reached significant energy reduction due the RES installations and proper controlling system.

Conclusion

The legal requirements based on directive [1] and rapidly increasing prices of natural gas and other fossil fuels force house owners to make deep modernisations of the houses. To reach the aim not only thermo modernisation but also the renewable energy sources are needed.

Using different installations of RES in the building is much more effective if the proper program coordinates those of different systems to always reach the highest efficiency by the management of the renewable energy sources.

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Mercury removal from flue gases by adsorption processes using carbon-based sorbents

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Keywords: mercury removal, adsorption, environmental pollutants, activated carbon, coal combustion

ABSTRACT

Mercury vapours and compounds are particularly hazardous environmental pollutants (HAPs-Hazardous Air Pollutants), according to the U.S. EPA [1]. The World Health Organization (WHO) has identified mercury as one of the 10 chemicals of major public health concern due to its high toxicity [2]. In the past, Europe used and emitted large amounts of mercury. However, over the last 20 years, significant legislative action, for example, limiting or banning the use of mercury and imposing limits on emissions, has significantly reduced the use and release of mercury into the environment. The contributions by the most important sectors (according to the EEA classification) to mercury emissions in the European Union (year 2018) are energy supply (41%) and manufacturing and extractive industry (42%) [3]. The EU countries with the highest total mercury emissions into the air are Poland and Germany, 8.74 tonnes by Poland and 8.25 tonnes by Germany (fig. 1). This is due to the fact that these countries base their electricity generation mainly on the combustion of subbituminous and lignite coals.

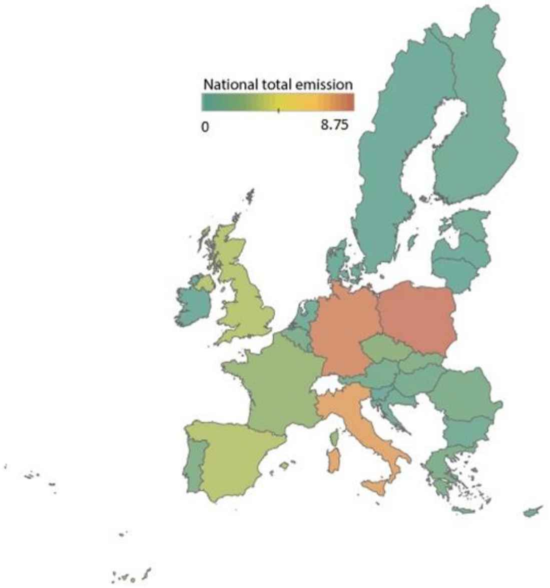

Figure 1. Total amount of mercury emitted in 2018 by EU-28 countries - map [3]

During combustion, the mercury in the coal is decomposed into three different species: particle-bound mercury (Hg^p), vapour-phase elemental mercury (Hg^0), and vapour-phase

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oxidized mercury (Hg^{2+}) [4]. The conversion of mercury from one form to another is important for the selection of an effective mercury removal technology. Mercury emission control technologies are still relatively new compared to SOx and NOx emission control ones, which have been commercially available for at least three decades. Adsorption processes using materials such as activated carbons [5], zeolites [6] or geopolymers [7] are promising for the removal of low concentrated Hg present in coal combustion flue gas streams. Therefore, it is necessary and important to identify effective sorbents for mercury removal and to understand the mechanism of mercury sorption. Activated carbons, the most commonly used sorbents, have been proved to remove mercury from flue gas in the laboratory and in commercial-scale tests [8]. The capture of mercury on carbon-based sorbents are dependent upon the temperature of the system, the concentration of mercury in the flue gas, textural properties, chemical and physical characteristics of the sorbent surface, as well as the particle size of the sorbents and the flue gas composition.

This study discusses mercury adsorption on carbon-based sorbents in the context of its removal from flue gases. As a result of the mercury adsorption tests carried out in the fixed bed reactor, breakthrough curves were obtained, which allowed determination of the maximum mercury sorption capacity of the materials and their applicability to technologies controlling mercury emissions using sorbent systems. In order to use appropriate sorbents, porous texture characteristics are required and essential. The porous texture of all samples was studied based on N_2 adsorption/desorption isotherms at 77 K and CO_2 adsorption isotherms at 273 K using an Autosorb-1-C static volume analyzer (Antonpar Quantachrome Instruments, USA). The textural parameters such as the BET surface area, micropore volume, mesopore volume and PSD were determined and their interpretation and effect on mercury sorptions was discussed. In addition, the effect of surface properties was identified. The surface chemistry of the materials under study was analyzed using the Boehm titration method to quantify organic oxygen-containing surface functional groups. On the basis of the correlation matrix, a strong correlation was found between the volume and surface area of the mesopores to the maximum mercury sorption capacity. It may be presumed that the presence of mesopores play an important role not only as transport networks but also make a significant contribution for mercury adsorption. The influence of the oxygen functional groups on the mercury sorption capacity was found to be determined by the content of the lactone groups. It was generally assumed that the Hg^0 removal was usually identified as a synergistic contribution of physisorption and chemisorption.

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Influence of SnO_2 addition to durability of nanoframes canatalysts for ethanol electro-oxidation reaction

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Keywords: Nanoframes, SnO_2 nanoparticles, SnO_2 layer, durability

ABSTRACT

When designing anodic catalysts for ethanol oxidation reaction (EOR) for direct ethanol fuel cell applications (DEFC), four main parameters must be considered: shape, structure, size, and chemical composition. All these parameters could be controlled during the synthesis of the nanocatalysts. The shape of the catalytic nanoparticles is one of the most important factors affecting EOR because ethanol oxidation (like other catalytic reactions) occurs on the surface of the nanocatalysts. Nanocatalysts with different shapes expose different crystal planes on the surface, e.g., cubic nanoparticles expose {100} surfaces, while tetrahedral nanoparticles expose {100} planes on surfaces. These differences strongly affect the catalytic activity toward EOR. On the other hand, the size of the nanoparticles is also crucial for catalytic applications, it is generally accepted that small nanoparticles are more active than their larger counterparts. Moreover, to obtain nanocatalysts with the highest activity, the chemical composition must be carefully chosen. Generally, the majority of anodic catalysts for DEFC are Pt-based however, to increase the selectivity and durability, platinum is often doped with other metals such as rhodium, tin, ruthenium, or nickel. In addition, it is crucial how these elements are mixed and arranged, for example, it is possible to obtain PtSn nanoalloy, but on the other hand, it is possible to obtain Pt nanoparticles with attached Sn nanoparticles. In both cases nanocatalysts will be composed of platinum and tin, however, they will exhibit different catalytic properties toward EOR.

In this work, two different PtRhNi/SnO_2 nanoframes-based catalysts are obtained. The first consists of PtRhNi nanoframes covered with small, about 3 nm, SnO_2 nanoparticles (PtRhNi/SnO_2 NPs); and the second is the PtRhNi nanoframes covered with a thin and incomplete SnO_2 layer (PtRhNi/SnO_2 TL). Both nanocatalysts were tested toward ethanol oxidation reaction (EOR) and show higher activity in comparison to PtRhNi nanoframes without SnO_2 (PtRhNi NFs) addition and commercially used Pt nanoparticles. Especially, the electrochemical durability and stability of obtained nanocatalysts were tested. It was shown that both PtRhNi/SnO_2 nanoframes-based catalysts develop similar mass and specific activity, as well as nearly the same onset potential, but their stability is significantly different. It turns out that catalyst based on PtRhNi nanoframes covered with a thin SnO_2 layer is susceptible to degradation, while the catalyst consisting of PtRhNi nanoframes covered with SnO_2 nanoparticles is much more durable and could be used as an efficient catalyst toward EOR.

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Catalytic performance of Fe-modified delaminated zeolite in selective catalytic reduction of nitrogen oxides with ammonia

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Keywords: DeNO$_x$, MWW zeolites, iron catalysts

ABSTRACT

Selective catalytic reduction with ammonia (NH_3-SCR) is among the most efficient methods used to abate the emission of nitrogen oxides from stationary sources [1]. However, the commercial catalyst of NH_3-SCR shows satisfactory activity only in a narrow temperature range. Moreover, the active phase of the material, V_2O_5, oxidizes SO_2 to SO_3, which causes emission of secondary pollution, deposition of ammonium or metal sulfates, and ultimately, deactivation of the catalyst [2].

According to the literature [1,3], the most active catalysts of NH_3-SCR exhibit high surface acidity and well-developed pore structure. One of the examples of such materials is ITQ-2, delaminated zeolite belonging to MWW family. Acidity of this aluminosilicate can be tailored by the optimization of Si/Al molar ratio, while irregular arrangement of the MWW layers provides very high specific surface area of ca. 700 $m^2 \cdot g^{-1}$. Additionally, it was confirmed that transition metals, such as iron are the most advantageous to substitute toxic vanadium as the active phase. The beneficial effect of Fe was ascribed to its participation in the redox cycle and delivery of acidic sites of Lewis type [4,5].

Despite the interest in the application of many types of zeolites in NH_3-SCR, only few studies have considered Fe-modified ITQ-2. Therefore, our study aimed to explore the influence of the modification method on the catalytic performance of Fe-ITQ-2 in NO reduction. Iron was introduced into the framework of the delaminated zeolite on the synthesis level (one-pot synthesis) or by post-synthesis modification. The support and the catalysts were characterized using ICP-AES, XRD, low-temperature N_2 sorption, TPAD, and UV-vis. The catalytic reaction was conducted using model gas mixture in the temperature range of 150-450 °C. We have observed that direct incorporation of iron resulted in the formation of well-dispersed iron cations, which shifted the temperature window to lower values. However, the method of Fe introduction did not noticeably influence the amount of N_2O produced during the reaction and for both catalysts concentration of nitrous oxide did not exceed 15 ppm in the entire investigated temperature region.

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Study on combustion of ammonia/gaseous fuels mixtures in flameless combustion process

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Keywords: ammonia, flameless combustion, furnace, nitric oxides emission

ABSTRACT

The coronavirus pandemic economical disturbances, together with the complicated geopolitical situation caused by Russia's invasion of Ukraine, have significantly altered the energy market in the European Union and worldwide. In addition to a significant increase in the price of basic energy sources such as natural gas oil and coal, their availability has also decreased, particularly as a result of the introduction of the fuel embargo from Russia and the need to create new trade routes. This has contributed to a reduction in the security of supply of energy carriers and consequently, electricity. In parallel, due to the high prices of fossil fuels, the profitability of production of alternative carriers has improved, including renewable fractions derived biomass as well as the use of locally available municipal waste. it has enabled the implementation of technologies to produce synthetic fuel streams [1], based on the use of synthetic gases of various origins. These technologies are based on a range of thermo-chemical and physico-chemical processes that have been used industrially for decades [2]. With high crude oil prices, they are becoming an alternative to crude oil derivatives, through their implementation for the production of hydrogen and synthetic gases from renewable sources[3]. Ammonia, produced from green hydrogen[4], is a promising high energy density alternative in relation to the direct use of hydrogen in industry. This work concerns the use of ammonia co-combustion with a stream of gaseous fuels of a wide composition spectrum covering low and high heating values.

Combustion was carried out with the use of high-temperature industrial combustion burner (flameless combustion burner), modernized for the combustion of low heating value gases, with the heating of air of the HRS type (High-cycle Regenerative System). The device was tested at constant 150 kWth firing rate and constant fuel bulk velocity of 85m/s. The use of a regenerative burner allows for heating the supplied air to a temperature above the auto-ignition temperature of individual flammable components of the gaseous fuel. In the conducted research, this temperature exceeded 1200K. The effects of air equivalence ratio, fuel composition and volume share of NH_3 in the fuel were investigated.

The experimental study included emission measurements of the combustion of these fuels and the determination of the temperature distribution and the level of emission of toxic substances inside the chamber. The tests have been performed for three mixtures: almost stoichiometric $\varphi=0.95$ as well as with equivalence ratio of 0.75 and 0.85. The composition of fuels has been selected to cover a wide range of calorific values from 6 to 35MJ/Nm^3), various generation technologies of these gases and the effect of increasing amounts of selected components. A stream of ammonia ranging from 0.5 to 10% by volume was fed to each of the mixtures. The composition of utilized fuels is presented in Table 1.

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Table 1. Fuel composition

Name of fuel	CO [% vol.]	CO_2 [% vol.]	CH_4 [% vol.]	H_2 [% vol.]	N_2 [% vol.]	NH_3 [% vol.]	LHV [MJ/Nm^3]
M100	0	0	100	0	0	0-5	34.7
Biogas	0	30.0	70	0	0		25.8
SG01	7.6	55.2	11	11.7	14.5	0-10	6.2
SG02	7	5	27	52	9		16.2
SG03	20	8	32	40	0		18.3

For combustion of synthetic fuels, a clear effect of oxidant content on the emission levels of nitrogen oxides was observed. The lowest emissions were measured for a combustion process characterized by an oxygen level in the dry flue gas equal to 1% (φ=0,95) for the fuel with the lowest calorific value and containing dominant inert gas content (SG01) and reached 100ppmv. An increase in the proportion of NH_3 for all fuels resulted in increased NO emissions, with the largest gradient observed for blends with 1 and 2% NH3 content. Further increases in ammonia share resulted in a reduction in the conversion of fuel nitrogen to NO. Further increases in ammonia share resulted in a reduction in the conversion of fuel nitrogen to NO. This is particularly evident for fuels SG01 and SG02. In the case of fuel SG01, for which the combustion temperature reaches the lowest values, this promotes the reduction of NO formed in the first phase of combustion by radicals formed from the decomposition of NH_3, according to the mechanism described by Miller mechanism reactions [5,6]. There is a clear relationship between the amount of combustion air supplied and the level of emissions. The less it is, the lower the nitrogen oxide emissions. Increasing the share of inert gases influences the NO emission level in three ways, concerning flammable components share, the share of ammonia and the equivalence factor.

The conversion factor (CF) was calculated to describe intensification of nitrogen bounded in ammonia to NO formation. It was concluded that the conversion of ammonia to fuel nitrogen oxides NO strongly depends on the amount of air supplied for combustion. The lowest value of the conversion factor of ammonia to nitrogen oxides was measured for a 1% oxygen content in the exhaust gas, representing typical volumetric combustion conditions. For example, for NH3 content in the fuel equal to 5%vol. and an equivalence ratio equal to 0.95, the CF coefficient was only 0.3% for SG02 fuel, 0.9% for biogas, and only 2% for methane (M100). However, a negative effect of the low proportion of oxygen in the exhaust gas on carbon monoxide emissions was observed.

It was noticed that relationship between ammonia content and its conversion to NO is not linear. It drops as the share of ammonia in fuel increases due to the reduction phenomenon of NO formation by amine radicals coming from fuel decomposition, especially in low temperature regimes.

The use of volumetric combustion technology for synthesis gases allows to obtain low emission levels of toxic substances. The results of the conducted research showed that ammonia can be used as an energy carrier successfully when co-firing in the volumetric combustion technology in industrial furnaces while maintaining low nitrogen oxide emissions.

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Mathematical modelling of cross-flow tube heat exchangers

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Keywords: cross-flow heat exchangers, semi-numerical modelling methods, non-linear models, four-pass steam superheater, experimental verification

ABSTRACT

Cross-flow tube heat exchangers are exchangers that are very widely used in many industries, including heating, ventilation and air conditioning (HVAC). They are also used as car radiators in internal combustion engines and air heaters in cars [1,2]. High-temperature cross-flow heat exchangers, i.g., superheaters and economisers, are commonly found in small and large steam and water boilers. Simplified methods, such as the method based on the logarithmic mean temperature difference of the two factors (LMTD), ε-NTU and P-NTU, are used for design and operational calculations. Formulas and diagrams for the calculation of cross-flow heat exchangers using the methods mentioned above are only available in the literature for a limited number of exchanger designs [1,2]. In all three methods, LMTD, ε-NTU, and P-NTU, it is assumed that the physical properties of the media, including the specific heat of both media, are independent of pressure and temperature. It is also not possible to calculate the local temperature changes of the tube walls along the fluid flow path, which is often needed for the correct selection of heat exchanger tube materials. The local temperatures of the two fluids and the tube walls can be determined by developing numerical or semi-analytical methods for the design and performance calculations of the exchanger [3-10]. Transient modelling of tubular cross-flow heat exchangers is the subject of a paper [11]. In works [3-5], the finite volume method was used to model cross-flow tube heat exchangers. The average fluid temperatures in the energy balance equation for a single finite volume were calculated as arithmetic means of the inlet and outlet temperatures in a given finite volume. The fluid temperatures at the control volume nodes were determined using the Gauss-Seidel method. In work [6], the average temperature of fluid flowing transverse to the tube axis was calculated in a given control volume as an integral average over the tube row. Using the mean integral temperature increased the accuracy of determining the temperatures of the fluid flowing transversally to the tube axis.

Semi-analytical calculation methods for tubular cross-current heat exchangers are presented in works [7-10]. As in the numerical methods, the entire heat exchanger is divided into finite volumes inside which the fluid temperatures are determined by exact analytical methods. As a result, the number of finite elements into which the heat exchanger has to be divided for adequate accuracy is lower than in the classical finite difference or finite volume method. Furthermore, it is not necessary to solve large systems of equations to determine the fluid temperatures at the nodes of the control volume. The advantage of the methods presented in the works [7-10] is that the temperatures of both fluids can be determined in a non-iterative manner. They are particularly suitable for the design and performance calculations of steam superheaters in boilers with subcritical and supercritical pressures. A typical feature of superheaters is the usually complex flow system and the strong dependence of the specific heat of the steam on pressure and temperature. Computer calculation times can be reduced by up to a dozen times compared to classical numerical methods used in heat exchanger modelling. The unsteady temperature distribution of the fluids in a cross-flow heat exchanger (car radiator) was determined using the finite volume method in work [11].

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Impact of Fit for 55 and RepowerEU proposals on power generation sector in Poland

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Keywords: Fit for 55, climate goals, modernization fund, decarbonisation

ABSTRACT

Fit for 55 proposal, as a set of complex regulations in a way of implementation of 55% emission reduction is a step in a proper direction, nonetheless, it raises some concerns:

- revision of the EU ETS Directive
- the proposal, instead of compensating for the shortages in the distribution of emission allowances under the EU ETS, by 2030, may increase the disproportions even more.
- Poland's energy transformation will require significant investment outlays, which, according to PKEE's estimates, will reach EUR 136 billion by 2030 - i.e. 4 times more than the amount of currently available national and EU funds for the decarbonisation of the Polish economy
- the Modernization Fund should be larger - in proportion to the new climate goals.
- eliminating the possibility of implementing investments in high-efficiency cogeneration fired with natural gas in central heating systems from the Modernization Fund, which may take place from 2024 - does not support the transition process.
- the feasibility of implementing green gases by 2030 is questionable both economically and technically - new reduction targets are difficult to achieve for the heating and cooling sector.
- the proposed changes to tightening the criteria for the use of biomass may reduce the use of renewable energy sources, especially in the heating and cooling sector.

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Analysis of damages on the boiler in district heating plant

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Keywords: boiler failure analysis, CFD modeling, damaged pipes

ABSTRACT

The paper describes research work related to the failure of a natural gas fired boiler. The study was conducted on a 130 MWt water gas-fired boiler with a modular design and a small water volume of about 35 m3. This construction is intended to allow for quick start-ups and shutdowns. Two burners with a nominal output of 68.5 MW each were used in the boiler. The tested boiler failed by rupture of the second stage water heater ECO2 pipes in the first rows on the flue gas inflow side (Fig.1).

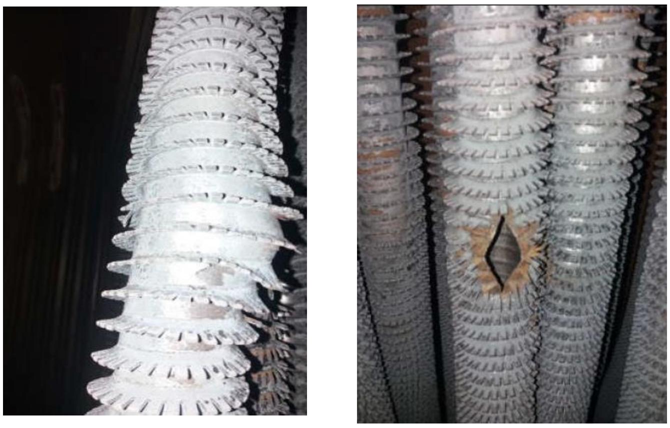

Figure 1. Visible deformation of the first and second row of the third stage water heater tubes

The ECO2 water heater, made of spiral finned tubes, was located just behind the boiler combustion chamber. The analyses performed indicate that the main cause of tube damage in the first row of the second stage ECO2 water heater was too high heat flow rate absorbed by the fins and tubes on the flue gas inflow side, both at high and low loads. The large differences in the temperature of the pipes and fins at their circumference, caused by the very strong radiation from the gas side, as well as by the vortices forming in the area at the back of the pipe, resulted in high stresses in the pipe wall (Fig. 2). At 100% load of the boiler, the temperature of the top of the fins reaches 614°C. The temperature of the top of the fins significantly exceeds the permisible temperature for the steel from which the fins are made. The wall temperature along the height of the fins decreases to 197 °C at the base, so the temperature drop over a fin height (distance of 12 mm) is $\Delta T = 417$ °C.

The high compressive stresses in the fin on the inflow side of the flue gas cause high tensile stresses in the pipe wall. When film boiling occurs, the wall temperature rises rapidly (above the material limit temperature). Under these operating conditions, failure due to creep can occur within hours, even at relatively low pressures of the flowing water.

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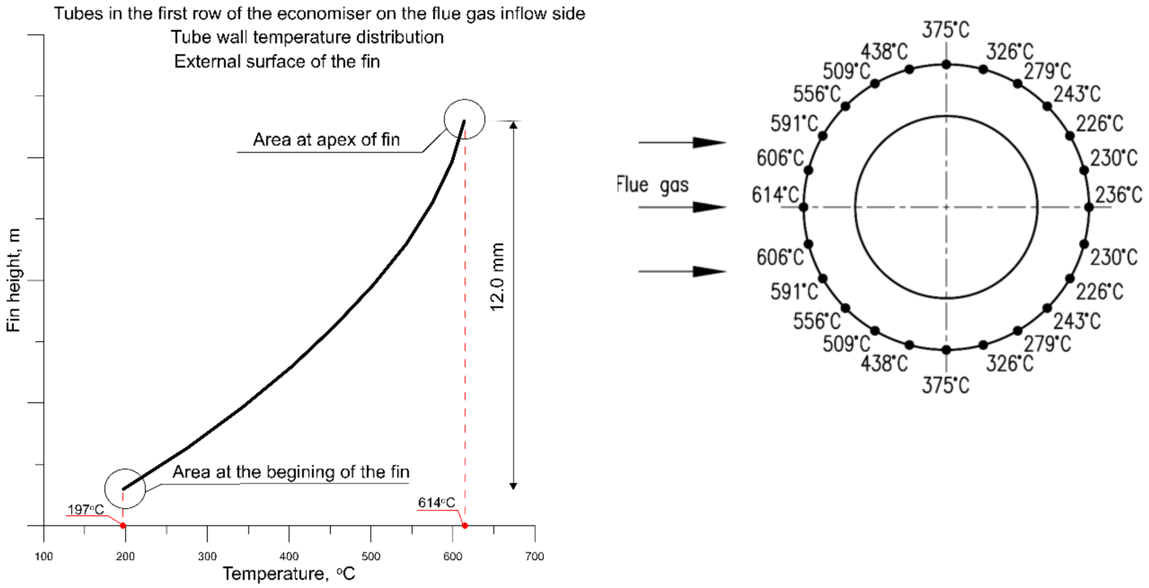

Figure 2. The temperature distribution of the fin.

To eliminate the causes of the failure, it was suggested to use plain tubes at least in the first two rows of ECO2 on the flue gas inflow side or to increase the value of water flow in the boiler heating spaces by increasing the mass flow rate of recirculated water. To control operating parameters of the ECO2 water heater, it is also recommended to measure the wall temperature of selected pipes in the first two rows on the flue gas inflow side.

Optimization of operation of building's electricity and heat supply system using renewable energy sources

Marcin Turoń[1,*]

Keywords: renewable energy sources, heat pumps, hybrid heating systems, control system

ABSTRACT

Europe is facing new challenges related to environmental pollution and rapid climate change. Heating systems used in housing construction often contribute to increasing pollution and greenhouse effect. In the face of the growing economic and environmental threat, it becomes necessary to develop new solutions targeting reduction of emission of pollutants and greenhouse gases. Only comprehensive solutions aimed at optimizing the use of energy, combined with the search for more ecological energy carriers, can prevent a global ecological catastrophe. Apart from environmental aspects, an important factor in the search for optimal energy solutions and their economical efficiency.

Research of building power supply systems with the use of renewable energy sources, conducted as part of the implementation doctorate, is aimed at developing of optimal solutions in terms of energy saving, economical efficiency and ecology impact. The tested power system is equipped with a photovoltaic installation, solar collectors, a ground heat pump, an air source heat pump, and a gas boiler, which is the peak source for the heating installation. The entire building power supply system is fully metered. The control system allows you to track functioning of individual devices, change their operating parameters, as well as archive and visualize measurement data.

The main goal of the research is to analyze the operation of heat pumps in order to determine which solution is more advantageous, especially in terms of their economical aspect. An important issue to be analyzed is an optimization of electricity consumption from a photovoltaic installation during its production. The research will be carried out over three complete heating periods, and the analysis of the measurement data will permit to develop guidelines for designers of installations for applying renewable energy sources in residential and other types of buildings.

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Hydrophobization of diatomaceous earth used to remove oil pollutants

Elżbieta Vogt[1],*, Karolina Topolska[1]

Keywords: hydrophobization, diatomit, oil polutions, stearic acid

ABSTRACT

The widespread use of petroleum substances causes the release of petroleum substances to the natural environment causing extensive contamination of soil, water and air [1-3]. For this reason, there is a need to remove petroleum pollutants from the environment. Various types of sorbents work well for this purpose, due to their non-toxicity, good price, wide selection and high efficiency [4-8]. The mineral sorbents are especially eagerly used to remove petroleum pollutions. Mainly there are: silicate minerals, zeolites, perlite, diatomite and clay rocks [9-13]. However, many sorbents are not resistant to moisture which limits their use. The hydrophobization process improves the effectiveness of sorbents used in a humid environment [5, 11-14].

The diatomite (DAMSORB produced by IM-POL [15]) was hydrophobized with methanolic stearic acid solution. The evaluation of the hydrophobic properties of the modified material was carried out on the basis of the results obtained from the tests: water absorption, floating on the water surface and the contact angles were determined. Oil and water absorption tests were carried out for both raw and modified samples. The carried out tests photos are showed at figure 1.

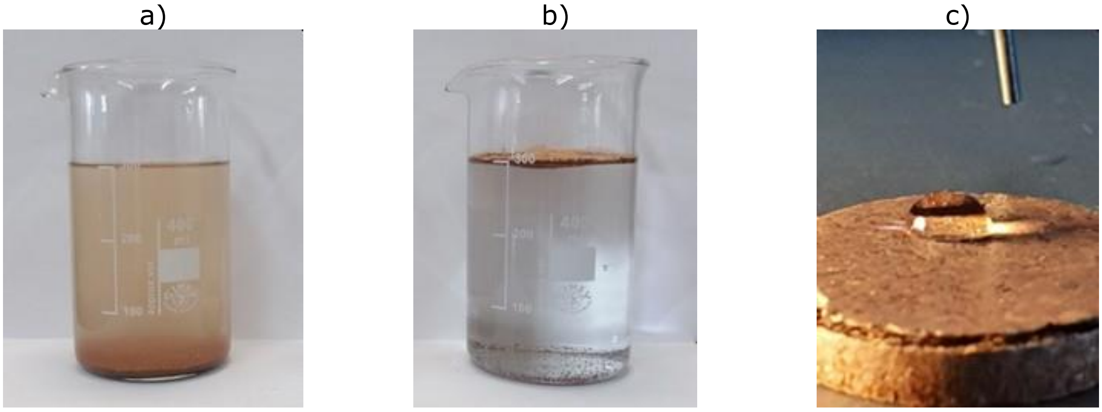

Figure 1. Photos of tests of evaluation of the hydrophobic properties: a, b) raw and hydrophobic material floating on the water immediately after placing the material on the surface, c) measurement of the contact angle

The modified samples are characterized by 30% lower water absorption than the raw material.

Examination of oil sorption from a water-oil mixture indicates an improvement in the sorption properties of the hydrophobized material in relation to the raw material. The obtained results are in table 1.

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Table 1. Average oil absorbency values

Material	Oil absorbency, % w/w
Raw	13,5
Hydrophobized	35,5

The oil sorption study carried out showed that the hydrophobized samples in the water environment have a higher absorption capacity in relation to oil contamination compared to the raw material. The hydrophobization process leads to an increase in the selectivity of the modified sorbent in the water environment.

The measurements of the loose and packed bulk density shows a slight decrease in the value of the bulk density of the hydrophobized sample in relation to the value for raw sample.

Table 2. Packed and loose bulk density values

Material	Bulk density [kg/m3]	
	Packed	Loose
Raw	612,2	552,4
Hydrophobized	583,8	532,7

Changing the density of the material in this direction is beneficial when using a sorbent to remove pollutants from water reservoirs.

Acknowledgments

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Kompaktowe stacje pomiarowo – integrujące All-in-One w ramach Systemu Zarządzania BMS Economic Health

Patryk Weisser [1],*, Andrzej Błachowicz [1]

STRESZCZENIE

W referacie przedstawiony został Automat pomiarowy do montażu w stacji pomiarowej rejestrującej komplet zmiennych środowiskowych wraz z układem sterowania służący do analizowania stanu środowiska naturalnego, takich jak:

a) temperaturę powietrza,
b) temperaturę promieniowania powierzchni,
c) wilgotność względną powietrza,
d) zawartość dwutlenku węgla w powietrzu,
e) prędkość powietrza,
f) natężenie oświetlenia,
g) ciśnienie atmosferyczne,
h) poziom natężenia dźwięku,
i) obraz (z kamery),
j) ruch (czujnik ruchu),
k) kierunek powietrza,
l) wysokość opadów
m) zanieczyszczenia powietrza, stężenia: pyłu (PM1.0, PM2.5, PM4, PM10), CO_2, NOx, SO_2, TVOC,

co w konsekwencji umożliwia realizację określania poziomu jego zanieczyszczenia, rejestrowania jak również sterowania parametrami wpływającymi na mikroklimat w obiektach użyteczności publicznej, przemysłowych, budynkach biurowych i mieszkalnych. Urządzenie może również służyć jako element rozproszonego systemu monitorowania stanu środowiska w miastach oraz aglomeracjach miejskich. Wówczas urządzenie pozbawione jest funkcji sterowania, a realizuje jedynie funkcję monitorowania.

Istotą rozwiązania jest jego kompleksowość i możliwość zgromadzenia w ramach jednego urządzenia kompletu informacji – które to tylko w ujęciu komplementarnym pozwalać mogą dalej na zaimplementowanie układów sterowania mikroklimatem pomieszczeń czy umożliwiać prognozowanie wielkości i sposobu rozprzestrzeniania się zanieczyszczeń.

Kolejnym ważnym aspektem jest umożliwienia zastosowania urządzenia nie tylko w infrastrukturach nowobudowanych, ale także w już istniejących obiektach. Zazwyczaj urządzenia do komunikacji wymagały łączności poprzez sieć GSM z kartą SIM czy sieci LAN lub opcjonalnie WiFI. Pierwszy sposób związany jest jednak z kosztem utrzymywania kart SIM i nie w każdym miejscu istnieje odpowiedni zasięg, drugie rozwiązanie powoduje konieczność zbudowania sieci teleinformatycznej. Autorzy rozwiązania proponują, zatem wykorzystanie do transmisji danych i komunikacji nowe standardy rynkowe, jak:

- komunikację poprzez sieć elektryczną z wykorzystaniem standardu Power Line Comunication (PLC)
- komunikację drogą radiową poprzez popularny standard Z-Wave (co dodatkowo umożliwia także podłączenie kolejnych czujników lub urządzeń komunikujących się w tym protokole)
- komunikację z wykorzystaniem bezprzewodowej technologii Internetu rzeczy NB-IoT.

I ostatnia kwestia, która jest także istotna z punktu widzenia komplementarności

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systemu to możliwość sterowania instalacjami wentylacji, klimatyzacji, ogrzewania dzięki uzyskanym danym pomiarowym z wykorzystaniem wskaźników PMV i PPD komfortu termicznego.

Kwestia komfortu termicznego w pomieszczeniach biurowych jest od wielu lat przedmiotem norm: PN-78/B-03421: Wentylacja i klimatyzacja. Parametry obliczeniowe powietrza wewnętrznego w pomieszczeniach przeznaczonych do stałego przebywania ludzi oraz PN-EN ISO 7730:2006(U): Ergonomia środowiska termicznego.

Microplastic content in stabilized sewage sludge

Jagoda Worek [1], Ewa Gawlak[1], Kamil Kawoń[2], Joanna Chwiej[2], Katarzyna Styszko[1,*]

Keywords: microplastic, sewage sludge, environemtal, fertilizers

ABSTRACT

Microplastic is a small piece of plastic that is a disadvantage of mass production and poor storage[1]. Over the years, plastics in ecosystems have released mirkoplastic[2]. This is a global problem. Actions to counteract the emission of micro-particles to the environment are insufficient. Wastewater treatment plants, which are designed to remove pollutants, are not adapted to their elimination[3]. Scientists find newer and newer sources from which a huge amount of them is released[4], [5]. In the conducted research, stabilized sewage sludge was analyzed, which is used for the production of sewage fertilizers and reintroduced into the environment.

Samples from the wastewater treatment plant at the turn of June and July were analyzed for their microplastic content. For this purpose, density separation using saturated high-density salt was applied and the matrix was eliminated with hydrogen peroxide (H_2O_2). The separated fragments were analyzed by ATR FTIR infrared spectroscopy. Photographs of microplastics were also made using a Raman confocal microscope (Fig.1). The analyzes showed a high content of microplastics in the samples, ranging from 1,500 to 3,500 particles per 100 grams of dry weight (Fig.2). The most frequently detected plastic was LDPE. It constituted over 80% of all polymer fractions. The research showed that the stabilized sewage sludge from which fertilizers are produced is heavily contaminated with microplastics. Processes converting sewage sludge to fertilizer are not able to eliminate microplastics. Based on the research, it can be concluded that fertilizers are an important source of microplastics emissions to the environment.

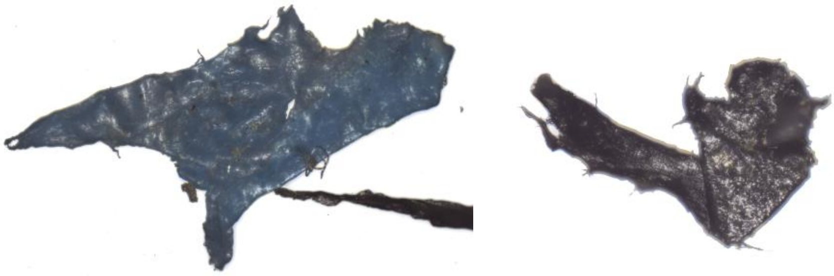

Figure 1. Microplastic separated from the samples

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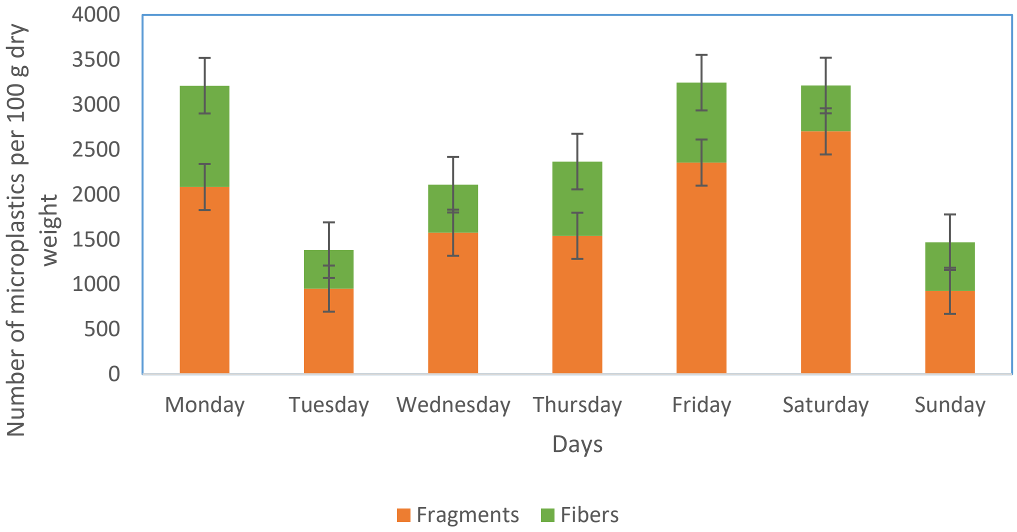

Fig.2 Microplastics content depending on the days of the week

The research showed that the stabilized sewage sludge from which fertilizers are produced is heavily contaminated with microplastics. Processes converting sewage sludge to fertilizer are not able to eliminate microplastics. Based on the research, it can be concluded that fertilizers are an important source of microplastics emissions to the environment.

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Analysis of the potential to increase Poland's energy security while giving up energy imports from Russia

Artur Wyrwa[1], Maciej Raczyński [1,*], Wojciech Suwała[1], Marcin Pluta[1], Janusz Zyśk[1]

Keywords: energy system, modelling, TIMES-PL, geopolitics, security

ABSTRACT

For several years, the TIMES-PL model developed by the AGH ESMLAB team has provided quantitative and qualitative results to support Poland's energy policy-making process. It belongs to the family of 3E (Energy, Economics, Environment) national energy system models built with the use of the IEA TIMES generator. Computer models of this class make it possible to carry out integrated analyses to plan actions in various areas of the energy system, on the supply and demand side, leading to the achievement of predetermined medium- and long-term goals. The best example of their effectiveness and measurable impact are EU regulations aimed at achieving climate neutrality developed with their extensive contribution, which are changing our daily lives. Models of this type play a very important role in designing the transformation of energy systems towards sustainable ones. This topic becomes even more prioritized in the context of the latest geopolitical situation and the deteriorating situation with energy imports to the EU from Russia.

The aim of the study was to analyse the possibility of strengthening Poland's energy security by increasing the use of domestic energy sources, diversifying energy supply, developing energy infrastructure, including seasonal energy storage facilities, and rationalizing energy consumption in the main sectors of the economy. An assessment was made of the feasibility of achieving net climate neutrality by 2050. This article discusses the structure of the TIMES-PL model and recent developments. On the supply side, current investment plans in the energy infrastructure, i.e., generation, transmission, and distribution, as well as plans to retire existing generating units, were considered. On the demand side, special emphasis was placed on the household and transportation sectors, as well as their possible integration with the power and district heating sectors using P2X and energy storage. The elaborated energy scenarios were discussed, outlining possible measures to improve the national energy security while giving up energy imports from Russia.

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Hydrogen storage - the experience of our research team

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Keywords: hydrogen, storage, adsorption

ABSTRACT

The current state of knowledge regarding hydrogen adsorption on carbon materials is highly developed. An important issue from the point of view of hydrogen storage is the appropriate choice of adsorbent. There are many papers in the literature on the sorption properties of carbon materials obtained from various precursors [1, 2]. While many of these materials are the subject of promising research, they have not been deployed on a commercial scale. Advantages with hydrogen storage through physisorption includes low system complexity, low pressure and fairly non-expensive materials [3]. Disadvantages include relatively low hydrogen density on carbon and the low temperatures required [4].

The paper presents the team's experience in obtaining adsorbents [5, 6] and also evaluates the possibility of using different types of materials in the context of hydrogen storage [7].

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Consideration of hybrid propulsion for an unmanned ground vehicles (UGVs)

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Keywords: UGV, hybrid propulsion, fuel cell, energy autonomy

ABSTRACT

Unmanned Ground Vehicles are mobile land platforms designed to work in various application. Nowadays UGV's are used in industry, e.g. intralogistics, mining, municipal, forestry and agriculture. Many constructions are also designed for defence applications, like logistic and pyrotechnic activities, supervision, reconnaissance, logistic support, medical evacuation and activities in the area contaminated with CBRN agents (chemical, biological, radiological and nuclear). Using remote controlled or autonomous robots allow to minimize exposure humans to hazardous.

Depending of usage scenarios mission requirements, additional equipment, navigation system and other effectors increase energy demand. Extending energy autonomy is becoming a key capability deciding on the operational capabilities of the UGV.

The conducted research focused on recognizing and identifying the potential and technological barriers in the application of electric drive solutions with hybrid power supply. Conventional fuels and fuel cells powered by hydrogen or its compounds are considered.

The energy density accumulated in the fuel, fuel availability, as well as the technical conditions of the required installation and safety of use are key parameters taken into account when selecting the technology.

The studies are focuses on the current possibilities and limitations of implementing fuel cells for medium UGV PIAP IBIS (fig.1) designed and manufactured in Łukasiewicz Research Network – Industrial Research Institute for Automation and Measurements PIAP, based on the latest scientific research and market research. Results are expected to be extended on new large UGV PIAP HUNTER (fig.1), which is under development stage.

Łukasiewicz Research Network – Industrial Research Institute for Automation and Measurements PIAP is professional supplier of Polish Explosive Ordnance Disposal robots for over 23 years both on the domestic and foreign market.

Figure 1. Unmanned Ground Vehicle produced by Łukasiewicz - PIAP (from left PIAP IBIS, PIAP HUNTER)

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Designing perovskites with in situ exsolution of nanocatalysts for boosting performance of symmetrical SOFCs

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Keywords: redox stable electrodes, in situ exsolution, nanocatalysts, symmetrical Solid Oxide Fuel Cells

ABSTRACT

Solid Oxide Fuel Cells (SOFCs) are among the most promising technologies for the production of electricity and heat from traditional and renewable energy sources. The energy generation by combustion of fossil fuels (coal, oil and the derivatives, natural gas) brings many serious environmental problems and the depletion of these fuels urgently requires the development of new alternative clean and green energy. Also, conditioned by the European political actions in the coming years, it is inevitable to increase the share of alternative, efficient sources of energy with limited negative environmental impact.

The main advantages of SOFCs are high efficiency and fuel flexibility. The application of SOFCs can also significantly reduce CO_2 emissions and other harmful gases (NO_x, SO_x, CO) when compared to traditional combustion technology. Symmetrical Solid Oxide Fuel Cells (S-SOFCs) with the same electrode, are very promising, due to reduced cell components, simplified manufacturing process and alleviated chemical stability problems, consequently decreasing production costs and ensuring a long-term stable operation [1-3]. S-SOFCs can also address carbon deposition and sulfur poisoning problems by simply reversing gas flows. In addition, S-SOFC facilitates a reversible operation between fuel cell and electrolysis mode. Since the S-SOFC concept was first proposed by a patent in 2001 [4], it draws a lot of intensive research. NASA has developed a S-SOFC design with good performance (~900 mw cm^{-2} at 850 °C) [5]. However, power outputs exceeding 1000 mWcm^{-2} of S-SOFCs are rather reported at high temperature range (≥ 800 °C). To be competitive, the commercial application of SOFCs will require lowering the operational temperature to a low temperature range (≤600 °C), while still maintaining a high-power output. To lower the operating temperature of S-SOFCs, redox stable electrode materials with enhanced electrocatalytic properties are indispensable for boosting the performance of S-SOFCs.

In this work, tungsten doped $SrFeO_{3-\delta}$ perovskites were obtained, and the maximum doping level of tungsten in $Sr_2Fe_{2-x}W_xO_{6-\delta}$ compounds was determined which is limited to x =1.0 ($Sr_2FeWO_{6-\delta}$). Structural properties, oxygen nonstoichiometry, transport properties data were measured for $Sr_2Fe_{2-x}W_xO_{6-\delta}$ (x = 0.1 to 1.0) perovskites. The substitution of tungsten in $Sr_2Fe_{2-x}W_xO_{6-\delta}$ oxides significantly affects the synthesis condition and crystal structure of investigated compounds. For instance, B-site rock salt-type ordered double perovskite $Sr_2FeWO_{6-\delta}$ (x = 1.0) with *P*21/*n* space group can only be synthesized at reducing conditions, while simple perovskite $Sr_2Fe_{1.9}W_{0.1}O_{6-\delta}$ (x = 0.1) with *Pm*-3*m* space group can be easily obtained in air. In this study, the synthesized single-phase $Sr_2Fe_{2-x}W_xO_{6-\delta}$ (x = 0.1-0.5) perovskites have been systematically investigated as redox-stable electrode materials for boosting the performance of symmetrical SOFCs. Phase composition, crystal structure, oxygen content, transport properties, chemical stability in

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relation to mostly used electrolytes and chemical stability of proposed materials under reducing/oxidizing atmospheres were studied. It has been found that $Sr_2Fe_{2-x}W_xO_{6-\delta}$ oxides are compatible with classical electrolytes (8YSZ, $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-d}$ and $Ce_{0.8}Gd_{0.2}O_{1.9}$). Among all the investigated $Sr_2Fe_{2-x}W_xO_{6-\delta}$ (x = 0.1-0.5) materials, $Sr_2Fe_{1.8}W_{0.2}O_{6-\delta}$-based symmetrical cell shows the lowest stable electrode polarization with Rp = 0.06 Ω cm2 at 800°C for over 100 h in air, while $Sr_2Fe_{1.6}W_{0.4}O_{6-\delta}$-based symmetrical cell has the best result under reducing conditions (5 vol.% H_2 in argon) with Rp = 0.5 Ω cm^2 at 800 °C for over 100 h. The in-situ exsolution of nanoparticles has been observed for $Sr_2Fe_{2-x}W_xO_{6-\delta}$ materials at reducing conditions.

Quasi-symmetrical SOFCs were constructed based on the selected electrode materials, and very excellent electrochemical performance was recorded, with 679 mW cm^{-2} at 800°C in wet H_2 and 451 mW cm^{-2} at 800°C in wet CH_4 (Fig. 1a). The in-situ exsolution of metallic iron nanoparticles with the size below 10 nm in the anode material (Fig. 1b) contributes to the high performance of constructed quasi-symmetrical SOFCs.

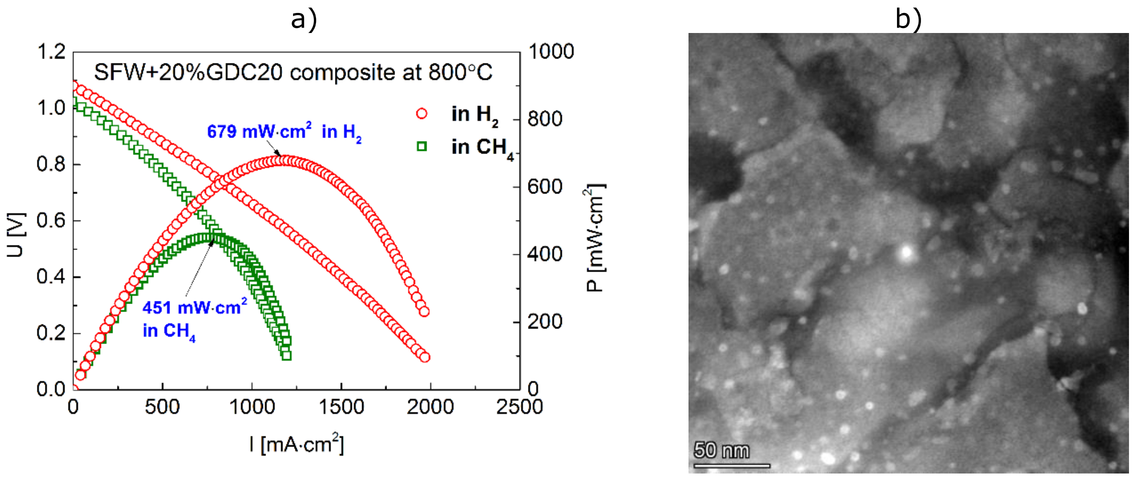
a)
b)

Fig. 1. a) Voltage and power density of quasi-symmetrical SOFCs in wet H_2 and CH_4, b) the in-situ exsolution of metallic iron nanoparticles imaged by STEM-HAADF.

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ITPE experience in the field of CCS/CCU

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Keywords: CO_2, CCS, CCU, SNG, methanol

ABSTRACT

Current theories and analyzes indicate a significant impact of the increase in CO_2 concentration in the atmosphere on the climate changes. The Polish economy currently emits over 400 mln Mg CO_2 annually. The actions taken around the world to reduce CO_2 emissions require the use of large-scale CCS/U (carbon capture and storage/utilization) installations in many sectors. Currently, post-combustion CO_2 capture technologies have the greatest chance of implementation in the energy sector. ITPE (former IChPW) has for years been carrying out a number of research works related to the removal and use of CO_2 captured from process gases, primarily in the energy and chemical industries, but also in the food industry and agriculture (biogas plants).

The technology developed by ITPE allows to achieve the degree of CO_2 capture at the level of 85-95%. The first Polish pilot installation for amine CO_2 absorption at ITPE enables the development of this process through the selection of new absorbents, process modifications and new equipment solutions. The research have been focused on lowering the energy consumption (main factor responsible for reducing the efficiency of units retrofitted with CCS systems). The results confirmed the possibility of reducing the energy consumption of the CO_2 capture process through the proper selection of the absorbent. Thanks to the use of a new absorbent it was possible to reduce the energy consumption of the process in relation to the reference solution (MEA). The new MEA-AMP-NMP-PZ and AMP-PZ absorbents showed a lower energy demand for regeneration by ~8-9% compared to 30% of MEA, ensuring 90% efficiency of CO_2 removal.

The energy consumption of CO_2 capture has also been reduced through technical modifications of the installation. They consisted primarily of the separation of the absorbent streams, as well as the introduction of interstage cooling, multi-stage absorber supply and heat recuperation in the desorber. Depending on the absorbent used and the process configuration, the heat consumption was reduced by 4-7%. The lowest value of the heat consumption (net) of 2.63MJ/kg CO_2 (world level) was obtained for tests with 30%/10% AMP/PZ solution in the configuration of separated streams with thermal integration, while for 30% MEA solution in the standard configuration was 3.13MJ/kg CO_2.

The experience gained resulted in the construction and commissioning of a demo installation for CO_2 capture in Łaziska Power Plant (TAURON) with a capacity of 200m^3/h (~400Mg CO_2/year) associated with a methane synthesis installation (SNG – synthetic natural gas). The most emblematic effect of ITPE work is the installation launched in 2019 at CIECH S.A., which allows to avoid emissions to the atmosphere of at least 5000Mg CO_2 per year. Laboratory work is currently underway on the synthesis of methanol with the use of CO_2 removed from the flue gas stream.

The CO_2 capture technology developed by ITPE harmonizes with the issues of H_2 economy - obtaining blue H_2 through the use of CO_2 capture in existing H_2 production plants. According to the EU strategy, blue H_2 will be of particular importance in the development of the H_2 economy during the energy transition.

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Reduction of NOx emissions during combustion of coke oven gas in a large combustion plant

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Keywords: NOx, coke oven gas, large combustion plant

ABSTRACT

Directive 2010/75/EU of the European Parliament and Council of November 24 on industrial emissions and Implementing Decision (EU) 2017/1442 of July 31, 2017 established conclusions on the best available techniques (BAT) for large combustion plants LCP (above 50 MW). According to them, the NOx content in the flue gases from coke oven gas from such installations should be lower than 100 mg / Nm^3. Although there are known solutions which are applied in the industry for reducing the content of NO_x to the required level for flue gases from coal and natural gas, there are no such solutions for flue gases from coke oven gas, which is specific due to its properties (including: water vapor, sulfur compounds, hydrogen cyanide, chlorine, alkali, tar hydrocarbons).

The NOx emission from Combined Heat and Power Plant (which is a large combustion plant LCP) located in ArcelorMittal Poland Zdzieszowice Coke Plant exceeds the limits established by the new regulations. The NO_x content varies from 207 to 409 mg/Nm^3, depending on the sampling point.

To meet the legal requirements, a project was launched aiming at the erection of an installation for reduction of NO_x content in flue gases from LCP.

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Examination of commercial V_2O_5-WO_3/TiO_2 catalysts for SCR application: laboratory tests and deactivation mechanisms

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Keywords: SCR, Power Plant, Catalyst, Deactivation, Poisoning

ABSTRACT

Power production plants utilizing solid fuels may take advantage of Selective Catalytic Reduction (SCR) method for nitrogen oxides mitigation. The presence of catalyst allows to conduct the reaction at much lower temperatures than in case of non-catalytic method. A widely applied catalyst in SCR installations is the V_2O_5-WO_3/TiO_2. For such catalyst, there are several mechanisms that can potentially increase the rate of its deactivation above the standard level. For SCR installations in power generation industry, the rate of catalyst deactivation may depend on the type of fuel that is used to produce energy. Catalyst activity, which is the ability of nitrogen oxides reduction, is related to the amount of ammonia adsorbed on the catalyst active sites. However, the latter can become inaccessible due to chemical poisoning and contamination. Alkali metals, such as sodium and potassium, are known for having the most damaging effect on the catalyst due to poisoning phenomenon. In this work, several samples of V_2O_5-WO_3/TiO_2 catalyst from coal-fired commercial power units have been examined. Parameters such as overall activity, SO_2/SO_3 conversion, specific surface area and chemical composition were presented, and outcomes were referenced to typical mechanisms of catalyst deactivation. Analyzed data allowed to determine a rate of deactivation for each catalyst, expressed as percentage of deactivation per hour of catalyst operation, which indicates that some catalysts loss their activity faster than others. The outcomes of the performed tests prove, that the major factor that leads to the catalyst deactivation is poisoning caused by high content of alkali metals, such as potassium and sodium, in the utilized fuel. The comparison between different solid fuels ash composition revealed, that some may contain much higher amount of alkali metals as well as chlorine than the others, can lead to the formation of gaseous KCl – the compound that can strongly affect the catalyst. Its formation is in turn related to combustion temperature and content of silica and alumina in fuel, which was also addressed in this work.

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