High-Temperature Processing and Recovery of Cu Catalyst Promoter

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The following article describes the results obtained from the plasma smelting reduction of a particular type of waste - catalyst with a Cu promoter. The catalyst is used for the process of a selective reduction of nitrobenzene ($C_6H_5NO_2$) to aniline ($C_6H_5NH_2$). The plasma smelting occurs in a reducing atmosphere. Six samples of the exhausted catalyst with a Cu promoter were used in the smelting process. The chemical composition of the promoter exhibited a presence of a wide range of elements. Fluorspar (fluorite) and calcium oxide (quicklime) were used as the slag-agent for the given testing. Reducing agent was the powdery graphite - waste from the manufacture of the graphite semi-finished product. The results of experiments, carried out at 80 kVA in the plasma reactor, proved that this type of catalyst can be, in fact, disposed of using the plasma technology. Recyclability of the metal contained in this waste is high; Cu ranges around 88%. Moreover, the article describes the chemical analysis of the slag, fly ash and the composition of synthesis gas in all samples of the processed catalyst.

Keywords: Waste, Catalyser, Cu promoter, Plasma technology

1 Introduction

In Slovakia and the Czech Republic, recently more attention is paid to the waste treatment using the thermal plasma. First results of experiments are available describing the outcome of the processes of high temperature waste treatment in the plasma reactor; for example in the area of municipal waste, fly ash from thermal power plants or from hazardous asbestos-based waste [1-4]. Technologies using the thermal plasma for the refining processes or for the processing and recycling of the scrap metal have been known for several decades, especially in the developed countries of North America, Western Europe and Japan.

Presently, the technology of plasma melting and gasification is developed mainly in the area of recycling and disposal of hazardous waste, radioactive materials, nuclear weapons, and also in refining high-purity substances.

Temperatures obtained from the low-temperature thermal plasma technology are currently the highest temperatures used in practice [5-7]. In such extreme temperature conditions the decomposition of larger molecules of the hazardous organic matter into atoms and radicals occurs. Moreover, if the high temperature melting takes place in reduction conditions and compliance with the prescribed methodology for the processing, the formation of the polycyclic aromatics does not take place.

Today, the results from the treatment of various industrial waste by plasma technology are well known [8]. The recovery rate of precious metals of various metallic waste is a focus of many articles and papers [9-12]. A separate domain of the plasma technology use is its inclusion within the liquidation process of catalysts [13]. In this area, as well, the results are well known as they were obtained under various conditions using the low-temperature thermal plasma [14-15]. A by-product of the waste processing is always synthesis gas and slag. The energy recovery from waste in the process of the high-temperature gasification by the low-temperature thermal plasma is described in the study paper [16-17].

In addition to the known technological processes of the pyro-metallurgical method for the recovery of precious metals from waste, there are also chemically based methods available. (ex. leaching). The basis of leaching method is the transfer of a given phase to the liquid phase. Bioleaching processes use micro-organisms or their metabolites, eventually. The bioleaching agents are microbial metabolites, organic acids in particular (oxalic acid, citric acid, etc.) [18]. Extraction of Cu, Ag, Au, and Pd in the leaching process in nitric acid is described in [19-20]. Recovery of silver by this method is 87 %, and 98 % for copper. Leaching of Cu, Zn and Pb from printed circuit boards (PCBs) using electro-generated chlorine and hydrochloric acid solution is described in paper [19-20]. Degree of recycling of the metal content depends primarily on time, temperature, current density and particle size distribution of the treated waste. Leaching of copper from the PCBs at the room temperature, in sulfuric acid solution, was studied in detail in [21]. Degree of oxidation of copper in the leaching process reached 100 %. Recycling of copper from telecommunication and information technology waste is described in [22]. By using air as the oxidant and ammonia-ammonium carbonate leaching solution, copper could be extracted with high recovery - more than 90 %, and high extraction selectivity - around 98 %. The same waste studies the paper [23]. Tested leaching agents include sulfuric acid, ammonia-ammonium carbonate and ammonia-ammonium sulphate solutions, with or without addition of hydrogen peroxide. The results show that ammonia leaching has high selectivity for copper, and it could serve as a first step to recover the copper content in the e-waste, which is one of the major valuable

metals. Copper with 98.9 % purity was obtained.

The present article presents the results of experimental tests performed at 80 kVA plasma reactor for selected types of catalyst from the chemical and petrochemical industry in the Czech Republic. This plasma reactor allows to process waste containing the following material:

- organic and plastic materials (textiles, wood, plastics and the like),
- non-combustible inert materials (glass, ceramics and the like),
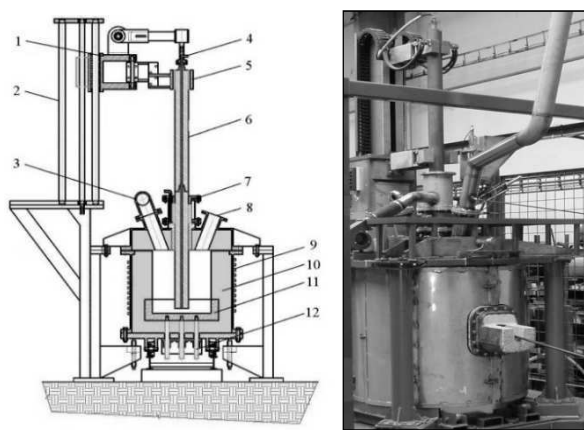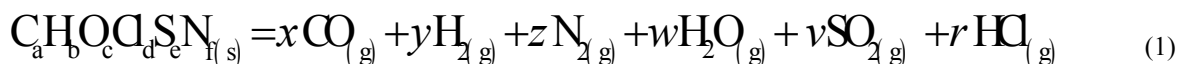- non-volatile metals (Fe, Cu, Al and the like),
- volatile metals (Hg, Cd, Zn, Pb and the like).

2 Study area

In the plasma reactor (Fig. 1) waste is melted and gasified as a result of plasma arc discharge, wherein the arc discharge is generated from plasma gas (argon, nitrogen, air, etc.). At such temperatures, independently of the partial pressure of oxygen, the organic and partly inorganic components of the waste are decomposing into simple gaseous and liquid compounds according to the general chemical reaction (1) [10]

$$C_aH_bO_cCl_dS_eN_{f(s)} = x\,CO_{(g)} + y\,H_{2(g)} + z\,N_{2(g)} + w\,H_2O_{(g)} + v\,SO_{2(g)} + r\,HCl_{(g)} \qquad (1)$$

Fig. 1 *Experimental plasma reactor*

(1-hollow graphite electrode sliding mechanism, 2-frame, 3-syngas outlet, 4-gas inlet – nitrogen for plasma arc generation, 5-cathode holder, 6-hollow graphite electrode – cathode, 7-water cooling system for cathode, 8-dispensing hole, 9-shell of the reactor, 10-lining, 11-furnace hearth – anode, 12-anode power supply)

The gaseous product is synthesis gas, comprising mainly hydrogen and carbon monoxide, with a low content of sulfur dioxide, hydrogen chloride and water vapor. Highly flammable gas, with no dioxins, furans and NO_x [22], [26] that by its composition resembles the reformed gas that used to be produced in the past in gas plants, can be used as fuel in cogeneration units for the production of electricity and heat. Synthesis gas may contain metal vapors with low boiling point; ex. Hg, Cd, Zn and Pb, which can be very effectively captured in the neutralization and filtering apparatus, together with the sulfur dioxide and hydrogen chloride. The non-gasified inert waste ingredients are melted to form two immiscible liquid phases on the bottom of the reactor - metal alloy and slag, which can be used in the metallurgical or the construction industry.

3 Analysis of the auto-catalysts melting process

Among waste that can be very difficult to recycle at the pyro-metallurgical production of copper and lead, are

industrial and auto catalysts. The reason is that the ceramic carriers of the catalysts are high in Al_2O_3, which sharply increases the melting point of the silicate slags. Such catalysts also contain carbon compounds, which are trapped therein in the process of use due to ongoing chemical reactions. The carbon compounds oxidize to carbon monoxide or dioxide, and thus are concentrated in the gas phase - synthesis gas [10].

The welding conditions of the given catalysts, adapted in such a way that the obtained products could be effectively used (material and/or energy use), can be defined based on the thermo-dynamic analysis of the multi-component system: Fe-Cr-Ni-Pb-Pt-Pd-Rh-CaO-SiO₂-Al₂O₃-MgO-CH (further MSC). Provided that only ceramic catalyst with carriers based on SiO_2, Al_2O_3, MgO, and CaO will be processed, then the appropriate flux (lime and fluorspar) is going to be used. The components, whose concentration is very low (Ni, Pb, Pt, Pd, and Rh) are neglected, thus the MSC can be reduced to a system of Fe-Cr-CaO-SiO₂-Al₂O₃-MgO-C-H (further RS). Stabilities of the individual RS phases, obtained by the thermodynamic analysis, defines the paper [10]. The results are interpreted graphically within a coordinate system $\log p_{CO2}/p_{CO} - 10000/T$.

Provided that for the reduction of the metal oxide a solid reducing agent (coal or coke) is used, within the work area of the plasma reactor at a temperature of 1450-1500 °C the balanced composition of the gas phase, e.g. p_{CO2}/p_{CO} which corresponds to the Boudouard reaction, will stabilize. A prerequisite of this reaction is the sum of partial pressures of carbon monoxide and carbon dioxide equals to 10^5 Pa. Under these conditions, not only the metal melts but also the oxides of iron, cadmium, lead and zinc reduces, and components like CaO, MgO, Al_2O_3, and SiO_2 melts and oxide slag is formed. It is possible to describe the slag using the equilibrium phase diagrams of the system CaO-SiO₂-MgO or CaO-SiO₂-Al₂O₃. Moreover, a part of the reducing agent (carbon) is dissolved in the reduced iron according to the following reaction

$$C_{(s)} = [C]_{(raw\ iron)} \qquad (2)$$
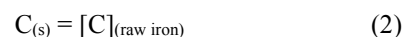
The reduced iron and molten slag based on CaO-SiO₂-MgO-Al₂O₃ are deposited on the bottom of the reactor as two liquid phases. Specifically heavier raw iron settles at the bottom of the reactor followed by a layer of a liquid,

specifically lighter, slag formed by the melting process of the slag-forming components contained in the feed substances. The slag may also contain a part of the unreduced iron oxides, mainly FeO, which, when the sufficient amount of lime is not added into the batch, may form a $2FeO \cdot SiO_2$.

At high temperatures, the reaction rates are extremely high. As a result, depending on the temperature and pressure, the thermodynamic equilibria takes place. Thermodynamic equilibrium of chemical reactions can be described by the following equilibrium constants [24]

Boudouard reaction

$$K_p = \frac{p_{CO}^2}{p_{CO_2} \cdot a_C} \qquad (3)$$

The reaction of methane

$$K_p = \frac{p_{CH_4}}{p_{H_2}^2 \cdot a_C} \qquad (4)$$

The reaction of partial oxidation

$$K_p = \frac{p_{CO}}{p_{O_2}^{1/2} \cdot a_C} \qquad (5)$$

The reaction of the complete oxidation

$$K_p = \frac{p_{CO_2}}{p_{O_2} \cdot a_C} \qquad (6)$$

Where:

p_i is the partial pressure of the i-th component in the system (CO, CO_2, O_2 and the like) [Pa],

a_C is the carbon activity in the system (if there is the reducing agent in the system in the solid state then $a_C = 1$).

During the treatment of hazardous and toxic waste may be produced a small amount of methane under certain conditions.

The effect of temperature on the equilibrium constants of the selected chemical reactions are graphically illustrated in Fig. 2 [25]. From the figure stems that the equilibrium of the endothermic reactions shifts with increasing temperature in the direction of the products. As for the exothermic reactions, e.g. methane CH_4, the equilibrium shifts with increasing temperature to the side of reactants.

If chemical reactions involve a change of volume, then, in that case, the equilibrium of chemical reactions is affected by the pressure. An example is the Boudouard reaction, where the increase in pressure is caused by the emergent carbon monoxide. Fig. 3 shows how the CO concentration decreases at the given temperature, when the overall system pressure increase from $p = 0.1$ MPa to $p = 3$ MPa [19]. The opposite situation takes place when methane is formed. The amount of methane at the pyrolysis of waste increases with the increasing pressure to produce energy-rich syngas.

The ratio CO/CO_2 in the reactor's atmosphere can be controlled by the added amount of the oxidizing agent in the form of oxygen, or water vapor, respectively. The steam reacts in the presence of carbon at high temperature according to the following reaction

$$2C + 3H_2O \rightarrow CO + CO_2 + 3H_2 \qquad (7)$$

In terms of the regulation of the reactor operation, the variable ratio CO/CO_2 is very important, because it determines the overall character of the environment in the reactor. Therefore, the formation of undesirable substances such as nitrate or NO_x is eliminated.
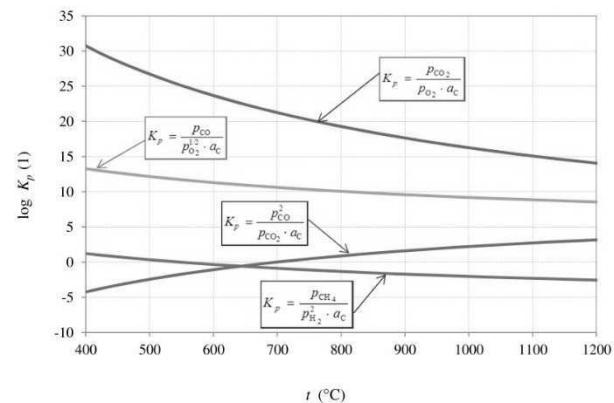

Fig. 2 *Equilibrium constants of the gasification reactions depending on temperature*
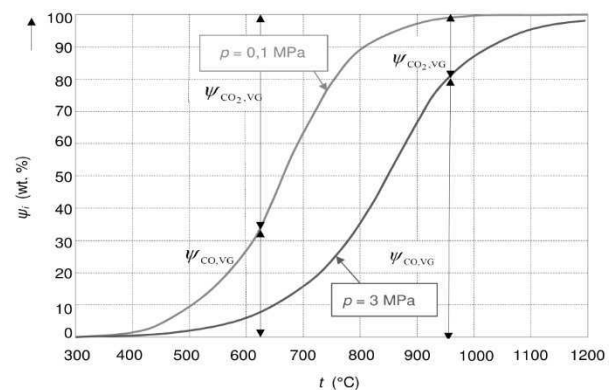

Fig. 3 *Equilibrium of the Boudouard reaction depending on pressure*

4 Experiment and discussion of results

For the purpose of this experiment, waste from the petrochemical industry - Cu catalyst promoter was treated in the plasma reactor of 80 kVA. Plasma arc discharge was generated as a dependent arc between the graphite electrodes. Temperatures of the gas atmosphere in the reactor are in the range of 1400 – 1500 °C. The experimental reactor of 80 kVA is designed so that the residence time of the synthesis gas in it is at least 2 seconds. Plasma reactor operates under the low vacuum that is regulated via suction blower with a variable speed.

4.1 Characteristics of Cu catalyst promoter

The catalyst with the Cu promoter is produced in the form of tablets of green-gray color with the diameter of 4.5 to 5 mm and height of 4.5 mm to 5 mm. The active components of the catalyst are compounds of copper, iron, magnesium and calcium. The basic component of the catalyst base is silica. In Tab. 1 is the chemical composition of a new, unused catalyst (ESM), as indicated by the manufacturer.

Tab. 1 Chemical composition of the new catalyst with the copper promoter

	Parameter	Value	Note
Content	CuO	min. 37.5%	DS
	SiO$_2$	36 – 40 %	DS
	MgO	3.5 – 5%	DS
	CaO	5 – 6.5%	DS
	Fe$_2$O$_3$	5 – 6.5%	DS
	Na$_2$O	max. 1%	DS
	Ni a Co	max. 0.015 %	DS
Annealing losses/600 °C		max. 7%	DS
Compressive strength		20 – 30 MPa, $s = \pm 4 – 6$	OS
Tapped density of powders		700 – 850 kg·m^{-3}	OS

Note: OS – in original sample, DS – in dry sample at 120 °C in spam of 2 hrs, $s = \pm 4 – 6$ is standard deviation

4.2 Use of a catalyst

The EMS catalyst is used in the selective reduction reaction of the nitrobenzene ($C_6H_5NO_2$) to aniline ($C_6H_5NH_2$). The reaction takes place in a reducing atmosphere, while the nitrobenzene passes at specific physico-chemical conditions through the catalyst bed, which accelerates the formation of aniline.

The used catalyst contains dangerous transition metals or their compounds. A mixture of the original tablets of the catalyst, sized 5 x 5 mm is black after its use. At the lower carbon content, the mixture has a reddish-brown color. In Tab. 2 is a typical chemical composition of the used catalyst with the Cu promoter indicated by the consumer – the producer of waste.

Tab. 2 Typical chemical composition of the catalyst – stated by the generator of the waste

Parameter		Value
Content	Cu	cca 30 %
	SiO$_2$	30 %
	MgO	16 %
	CaO	4 %
	Ni a Co	0.015 %
Content of the carbon sediments		max. 5 %
Powder density		650 – 800 kg·m^{-3}

Six samples of catalysts were chemically analyzed before their testing and the following composition was established:

0.1 –0.3 % Al$_2$O$_3$ 30 – 35 % CuO   0.5 – 10 % H$_2$O

13 – 26 % SiO$_2$ 1.5 – 2.5 % FeO   2.5 –3.5 % MgO

4 – 5.5 % CaO   0.001 – 0.002 %   10 – 15 % C

The given variance of chemical analysis clearly shows that the waste used for the experimental testing was not homogenous.

Catalysts with a copper promoter were mixed with the fluxes agents - lime (CaO) and fluorspar (CaF$_2$) before the melting process in the plasma reactor. The ratio of reagents and catalyst was designed according to the ternary diagram of CaO-Al$_2$O$_3$-SiO$_2$ in such way, that the slag melts at about 1300-1350 °C. Without the extra slag additives, the melting temperature of the catalyst base would range around 1600 °C, thereby increasing not only the energy demand of treatment per unit of waste, but it would also put a pressure on the resistance of the reactor lining to corrosion caused by the liquid slag. In the process of selection of slag forming ingredients, the chemical nature of the slag and the basicity were taken into consideration. The basicity was defined by the ratio

$$B = \frac{\% \, CaO + \% \, MgO}{\% \, Al_2O_3 + \% SiO_2} = 1 \qquad (8)$$

The reducing agent was added to the mixture of flux and the catalyst in a form of powdery graphite. Graphite powder originated from waste from the production of graphite semi-finished products. In this way, the reduction of metal oxides during the melting was ensured along with the decomposition of bound and unbound water contained in the catalyst of the reaction (7). The experiment was performed on six catalyst samples. Basic informations for input materials are presented in Tab. 3.

Tab. 3 Basic data of the input material and duration of the experiment using the catalysts with the copper promoter

Experiment	Catalyst (kg)	Slag forming additives (kg)	Redcution agent (kg)	Duration of the experiment (min)	Nitrogen Flow[*] (L·min^{-1})
1	43	6.25	0.41	300	8.5
2	64	5.00	1.00	375	8.5
3	62	7.50	0.50	425	8.5
4	108	8.40	1.17	415	8.5
5	54	4.21	0.59	305	8.5
6	43	5.40	2.80	405	8.5

[*] set at the 101 325 Pa and 25 °C

Tab. 4 indicates the summary of chemical analysis of products obtained in the plasma smelting reduction process. Analysis has shown that Fe, Ni, Cr and Si have partially reduced into Cu alloys. Silicon compounds were re-

duced from the slag melt due to the strong reducing conditions and the local overheating of the melt directly below the plasma arc. The last column of the table indicates the approximate recovery of a given non-ferrous metal - copper into the metal phase.

The chemical composition and the weight of the slag obtained from the individual experiments of catalysts smelting indicates Tab. 5.The table shows that the slag concentrate the elements with high affinity to oxygen, such as Al, Si, Mg, and Ca, but also a part of Fe in the oxide form of FeO and Cu_2O. Loss of copper in the slag

was very low. In addition to unreduced Cu_2O, small non-sediment metallic copper droplets were located in the slag.

These droplets represent the mechanical losses of a given metal in the slag, as demonstrated on the microphotograph of the refined microscope sample cut of slag (Fig. 4). Slag with high mechanical losses of copper is necessary to recycle through remelting. Debris were also subjected to the leaching testing. The test results confirmed that the slag is inert.

Tab. 4 *Chemical analysis and mass of alloys obtained from catalysts smelting*

Experiment	Cu alloy* (kg)	Chemical composition (%)					
		Cu	Fe	Ni	Cr	Si	Cu recovery in the metal phase (%)
1	11.2	96.5	2.10	0.40	0.20	0.80	89.89
2	17.0	87.0	12.0	0.00	0.30	0.70	82.65
3	16.5	90.0	4.50	0.15	1.12	4.20	85.66
4	28.0	97.8	1.21	0.03	0.20	0.70	90.68
5	14.0	95.3	1.49	0.05	0.55	2.15	88.36
6	11.2	96.2	2.70	0.10	0.40	0.50	89.61

* *the weight of the product situated in ingot mould, without cinsidering the mechanical losses*

Tab. 5 *Chemical analysis and mass of slag obtained from catalysts smelting*

Experiment	Slag* (kg)	Chemical composition (%)					
		CaO	MgO	SiO_2	Al_2O_3	Cu_{total}	Fe_{total}
1	27	28.59	7.96	47.80	5.46	0.62	3.24
2	36	30.82	8.42	48.05	5.19	0.38	4.70
3	38	31.52	7.84	47.95	5.42	0.49	4.33
4	57	34.81	8.54	49.35	3.61	0.32	2.31
5	30	33.59	7.76	47.35	9.27	0.20	1.81
6	26	34.42	6.01	49.44	2.49	0.51	2.55

* the weight of the product situated in ingot mould, without cinsidering the mechanical losses
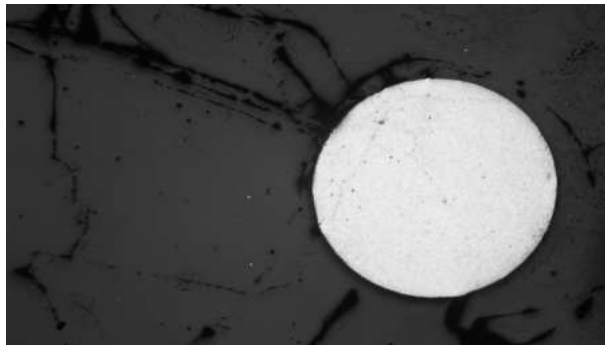

Fig. 4 *Micro-photograph of the refined microscopic sample of the reversible slag with the copper pellet*

Information about the mass of fly ash in each experiment provides Tab. 6. The table specifies the chemical composition of the fly ash, collected mainly in the cyclone, and subsequently in other filtration equipment.

Resulting from the chemical analysis, in addition to the oxides of CaO, SiO_2, MgO and Al_2O_3, mechanically stripped from the batch, and the unreacted carbon added to the mixture, the fly ash contained condensed metal vapors of Cu and Fe. The fly ash can be recycled without any problems, increasing the total recovery of metals.

Synthesis gas was discharged from the plasma reactor through a cyclone separator. Subsequently, synthesis gas

cooled rapidly in the hydrocyclone from temperature of 1500 – 1600 °C to temperature of about 160 – 170 °C. Remnants of the micro particles were subsequently caught up in a filter bag. In the next step, the acid components of the synthesis gas were neutralized in the countercurrent absorption column through the NaOH solution with pH = 9. From the absorption column, the synthesis gas led into the cooling system. Here, in the first stage the gas cooled below the dew point (60 °C) and the moisture was removed from it. Originally the synthesis gas was saturated through the cooling process in the hydrocyclone and by neutralization in the countercurrent absorption column.

The average concentrations of the main constituents of synthesis gas from the continuous chromatographic measurement of CO, CO_2, H_2, N_2 and CH_4 are specified in the summary Tab. 7.

After its cooling in the cooling system, syngas was reheated above the dew point, and subsequently mixed with natural gas and then burned in a cogeneration unit with a micro-turbine CAPSTONE C65. Electric and thermal energy was produced in the cogeneration unit. Thermal energy was acquired in the form of heating water through the exchanger surrounded by exhaust gas. Cogeneration unit operated with the fixed set-up of the required electrical power (55 kW).

Tab. 6 *Chemical analysis and mass of the fly ash originating from catalysts smelting*

Experiment	Fly ash (kg)	Chemical composition (%)						
		CaO	MgO	SiO_2	Al_2O_3	Cu_{total}	Fe_{total}	Annealing losses
1	1.2	16.16	2.32	17.55	12.83	8.86	4.77	13.73
2	2.0	9.61	1.04	11.57	18.22	20.43	7.01	22.13
3	1.0	21.07	1.16	19.77	17.72	25.52	1.83	15.00
4	7.2	10.82	1.99	12.13	17.98	45.54	3.01	7.09
5	2.0	16.61	2.81	17.77	13.09	9.64	5.99	16.00
6	1.0	11.13	2.17	9.05	15.55	21.04	7.00	19.30

Tab. 7 *Average values of main components of syngas during catalysts smelting*

Experiment	Syngas ($L \cdot h^{-1}$)	Average chromatography analysis (vol%)				
		H_2	CO	CO_2	CH_4	N_2
1	15.5	13.64	18.26	4.51	0.00	63.59
2	14.8	13.57	18.38	4.43	0.00	63.62
3	14.3	13.25	17.91	4.45	0.00	64.39
4	17.0	13.91	19.38	4.43	0.00	62.28
5	14.2	14.07	18.47	4.44	0.00	63.02
6	14.9	12.39	15.35	5.47	0.00	66.79

5 Conclusions

Due to the environmental problems associated with landfilling of the catalyst with the copper promoter, which causes irreversible loss of the metal content, new ways for its recovery and disposal are being explored. One method is the melting of the catalyst in the plasma reactor, wherein, the reduction of metal oxides in the metallic phase might occurs.

The recovery rate of copper in the alloy is at approximately 88%. The results of the analysis also shows that parts of Fe, Ni, Cr and Si were reduced in the copper alloys. The inorganic proportion of the batch, which is in the form of slag forming oxides of SiO_2, CaO, MgO and the like, concentrates in the liquid form above the metal phase by adding the fusing agent and meeting required temperature. The resulting slag, in addition to reducing the volume of the processed material, offers the possibility of its landfilling or its recovery in the construction industry due to its inertness.

Recovery of the copper from the catalyst with Cu promoter using the plasma smelting reduction is slightly lower (10 %), if compared to the recovery rate using leaching methods in different acids (nitric and sulfuric acid). From an environmental standpoint, the plasma technology is considered as the BAT technology. This is a great added value in comparison to other methods which produce waste that requires further treatment.

The first results from the high temperature smelting of the catalyst with the copper promoter suggest that the plasma technology is applicable in the process of disposal and recovery of such waste. In addition to the recycling of large metal content of the waste, this technology ensures that the waste, classified as hazardous, became suitable for landfilling or other use, without causing any substantial environmental impact.

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