Acta Mechanica Slovaca **23 (2): 56 - 61,** June **2019**
https://doi.org/10.21496/ams.2019.007

Acta Mechanica Slovaca
ISSN 1335-2393
www.actamechanica.sk

High-temperature Processing and Recovery of Decommissioned Electrochemical Cells and Batteries

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Abstract: The present article describes the processing and recovery of decommissioned electrochemical cells and batteries by means of high-temperature melting in a reducing atmosphere. The experiment was carried out using two samples weighing 15 and 20 kg. CaO was used as a slag-forming additive and carbon was used as a reducing agent. The results of the experiments carried out with an 80 kVA plasma reactor showed that the decommissioned electrochemical cells and batteries may be disposed of using the plasma melting technology and the resulting product may be further recovered. The recovery rate for the non-ferrous metal of interest (cobalt) is approximately 95 %. The article also presents the chemical analyses of the formed alloy about weight of 3.7 kg in first and 5.6 kg in second experiment. The vitrified slag and fly ash analysis was also performed. The volume production of syngas was 12 $m^3 \cdot h^{-1}$ with LHV from 2.7 to 3.4 $MJ \cdot m^{-3}$.

Keywords: *electrochemical cells, electrochemical batteries, high-temperature melting*

1. Introduction

The European Waste Catalogue code of the accumulators subjected to the analyses discussed in the present article is 16 06 05, Wastes not otherwise specified in the list – Batteries and accumulators [1]. Due to the fact that safe storage of electrochemical cells and batteries is problematic, they must be recycled or processed in a manner facilitating the recovery thereof. There are currently several known methods of disposal of electrochemical cells and batteries. The one that is most frequently applied is hydrometallurgical processing. However, also pyrometallurgical procedures are now being investigated. A pyrometallurgical method of waste recycling requires a relatively high amount of energy and high costs.

The first results of high-temperature processing of decommissioned LiMH cells and batteries [2] and other types of waste have already been published and they indicate the possibility to eliminate the problem associated with the storage of such wastes by applying the plasma melting technology; they also indicate that the materials and energy contained in such waste may be recovered. The above mentioned technology was applied in order to process, for example, the fly ash from the municipal waste [3, 4], electronic scrap [5], asbestos [6], or other waste materials, and subsequently use the separated waste components [7, 8, 9, 10, 11].

Nowadays there has been concern regarding scarcity of some materials, such as cobalt, used in electrodes [12]. Cobalt is costly, and manufacturers are moving toward lower cost and higher energy density materials to reduce the cost of battery manufacturing, while also seeking to improve safety and performance.

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Received: 2019.04.07
Revised: 2019.04.09
Accepted: 2019.05.28
Available online: 2019.06.15

Therefore, cobalt-free materials will be more attractive and cost-competitive eventually [13]. On the other hand, recovering cobalt at end-of-life and returning it to new battery production has the potential to reduce battery life cycle impact [13, 14, 15].

The article describes the results of the disposal of the mixed sample of electrochemical cells and batteries based on the use of the available environment-friendly techniques, the so called BAT (Best Available Techniques) in which the waste is disposed of and the contained materials and energy are utilised. The possibility of re-utilization of Co and other metal components represented in waste is discussed. The content of Co in the obtained alloy was more than 15 %, which, in view of increasing electromobility, can become an interesting secondary source of Co.

2. Experimental section

The experimental tests of melting and gasification were carried out using exhausted electrochemical cells and batteries taken from the separated collection of the commune systems in the Czech Republic. The chemical compositions of individual types of electrochemical cells and batteries are listed in Table 1.

Table 1: *Average chemical compositions of primary and secondary electrochemical cells[10].*

Component	*Content of component (%)*		
	Ni/Cd	*Li-ion*	*Ni/MH*
Steel	35	22	20
Li	-	3	-
Mn	-	-	1
Cd	15	-	-
Co	-	18	4
Ni	22	-	35
Zn	-	-	1
Al	-	5	-
Other metals	-	11	10
Alkali	2	-	4
Carbon	-	13	-
Plastics	10	-	9
Humidity	5	-	8
Other non-metals	11	28	8

The molten waste consisted of the same amounts of monocells and compact batteries in plastic cases manufactured by various manufacturers. Therefore, it can be assumed that the sample prepared for the experimental purposes was representative and reflected the real average chemical composition of electrochemical cells and batteries from the separated waste. The waste was molten and gasified in an 80 kVA plasma reactor (Figure 1) and the output quantitative and qualitative data regarding the by-product of the melting process, i.e. syngas, were continuously evaluated. CaO was used as a slag-forming additive for the charge and carbon was used as a reducing agent.

Fig. 1: *Photo of a 80 kVA plasma reaktor [10].*

During the melting process (at the temperature of approximately 1,600 °C), plastics, paper and electrolytes contained in worn electrochemical cells thermally decompose into simple gas compounds and carbon, according to the general chemical reaction [10].

$$C_aH_bO_cCl_dS_eN_{f(s)} = xCO_{(g)} + yH_{2(g)} + zN_{2(g)} + wH_2O_{(g)} + \\ + vS_{2(g)} + pCl_{2(g)} + rC_{(s)} \qquad (1)$$

where $C_aH_bO_cCl_dS_eN_f$ represents the general chemical formula of plastics, paper, and electrolytes; index (s) represents the solid phase; and (g) represents the gaseous phase.

The above presented chemical reaction indicates that during thermal degradation of plastics, paper, and electrolytes the combustible syngas (SG) is formed. As for combustible gases, SG will contain mainly carbon monoxide and hydrogen. Such gas may primarily be used in the reduction of metal oxides and secondarily, after being purified, as the energy gas (free of dioxins, furans and NO_x) in cogeneration units with a micro turbine for the production of energy and heat. The syngas purification process increases the total costs for more extensive practical utilisation of high-temperature waste processing. In spite of the fact that this process is regarded as very costly, it facilitates environmentally friendly waste processing and material and energy recovery.

The chemical properties of electrochemical cells and batteries indicate that these types of waste form a multi-component heterogeneous mixture containing metals and their compounds, carbon, plastics, electrolyte and non-metals.

Thermodynamic calculations and considerations were made on the basis of the assumption that used electrochemical cells would be melted in a plasma reactor, without any previous treatment, in highly reducing environment. This means that the used electrochemical cells would be melted with carbon being used as a reducing agent for the reduction of metal oxides.

Another assumption was that metal compounds contained in electrochemical cells would thermally decompose when melted in a plasma reactor, according to the following reactions:

✔ *Nickelous hydroxide ($Ni(OH)_2$) decomposes at the temperature of 230 °C to produce nickel oxide (NiO), according to the following reaction:*

$$\mathrm{Ni(OH)_2 = NiO + H_2O_{(g)}} \qquad (2)$$

When heated, manganese dioxide (MnO_2) decomposes according to the following reaction [9]

$$\beta\mathrm{MnO_2} = 525\ ^\circ\mathrm{C} = \beta\mathrm{Mn_2O_3} = 925\ ^\circ\mathrm{C} = \beta\mathrm{Mn_3O_4} = \\ = 1.180\ ^\circ\mathrm{C} = \gamma\mathrm{Mn_3O_4} = \text{over } 1.180\ ^\circ\mathrm{C} = \mathrm{MnO} \qquad (3)$$

On the basis of the comparison of the Gibbs free energy change per mole of reaction for oxides, fluorides and chlorides it may be assumed for aluminium and lithium compounds that at the temperature of 1873 K:

✔ *Aluminium chloride ($AlCl_3$) and lithium chloride (LiCl) would decompose to produce aluminium oxide (Al_2O_3) and lithium oxide (Li_2O);*

✔ *Lithium trifluoromethanesulphonate (CF_3LiO_3S) would decompose to produce lithium fluoride (LiF – melting point: 845 °C; boiling point: 1,676 °C) which may have the effects of a fluxing agent in slag, similarly to calcium fluoride (CaF_2). Carbon, oxygen and sulphur would pass into syngas and carbon may function as a reducing agent.*

In the production of metallic lithium applying the pyrometallurgical method, lithium oxide (Li_2O) and lithium fluoride (LiF) are reduced by aluminium, at the temperature of 1,050-1,100 °C, after adding calcium oxide (CaO), to produce metallic vapours of lithium, according to the following reactions [16]:

$$\mathrm{3Li_2O + CaO + 2Al = CaO \cdot Al_2O_3 + 6Li_{(g)}} \qquad (4)$$

$$\mathrm{6LiF + 4CaO + 2Al = CaO \cdot Al_2O_3 + 3CaF_2 + 6Li_{(g)}} \qquad (5)$$

Subsequently, reduced lithium would concentrate mainly in fly ashes due to its low boiling point (1049.0 K).

Melted and reduced metals with high boiling points would then concentrate on the bottom of the plasma reactor as a separate liquid phase - a metal alloy. The main components of the reduced alloy, with regard to the chemical composition of electrochemical cells, would include Fe, Ni and Co, whereas other metals, such as Cu, Sn, Mn etc., would represent minor components of the metal alloy – they would be present in lower concentrations. The phase equilibrium diagrams for Fe-Ni and Co-Fe systems indicate that the reduction temperature should range from 1,500 to 1,600 °C; at such temperatures, the Fe-Ni-Co alloy will be in the liquid phase. The melting point of the reduced Fe-Ni-Co alloy may decrease due to dissolution of carbon in the melt.

During the reduction-melting of electrochemical cells and batteries in a plasma rector, the following products are formed:

✔ ***Alloy,** located on the bottom of a plasma reactor, in which all metals with a high boiling point concentrate in a separate liquid phase, and are then reduced by carbon or metallically thermally, using Al and Li.*

✔ ***Slag** in which all metal oxides with high affinity to oxygen and slag-forming additives concentrate and where unreacted metal oxides dissolve.*

✔ ***Fly ash,** consisting of a mixture of mechanically pulled down charge particles and evaporated and condensed, or re-oxidised vapours of metals and their compounds that have low boiling points and high pressure of saturated vapours.*

✔ ***Syngas,** consisting mainly of a mixture of nitrogen, carbon monoxide, and hydrogen with low concentrations of water vapour, sulphur and chlorine. Syngas is primarily produced during gasification of plastics, paper and electrolytes, but also during*

reduction of metal oxides, using the carbon that is added to the charge as a reducing agent.

The proportions of charge materials for individual experiments with melting and gasification of exhausted electrochemical cells and batteries (ECaB) are summarised in Table 2. The table contains the data on the consumption of electric energy in a plasma reactor and the consumption of a plasma gas – nitrogen.

3. Results and Discussion

Table 3 contains the results of chemical analyses of the products obtained in the process of melting and gasification of electrochemical cells and batteries. The analysis results indicate that Fe, Ni, Co, Cr, Cu and Mn were reduced into the ***alloy.***

The chemical compositions of ***slags*** produced in the process of melting and gasification of waste electrochemical cells and batteries are summarised in Table 4. It can be seen that the slag contained the concentrated elements with high affinity to oxygen, such as Al, Si, Mg and Ca, as well as Fe in form of FeO oxides. The loss of Co in the slag was very low. In addition to unreduced Fe, the slag also contained unsettled particles of FeCoNi alloy (Figure 2), representing the mechanical loss of this metal in the slag, as well as graphite. Slags with high mechanical losses must be recycled by melting or magnetic separation of grind slags.

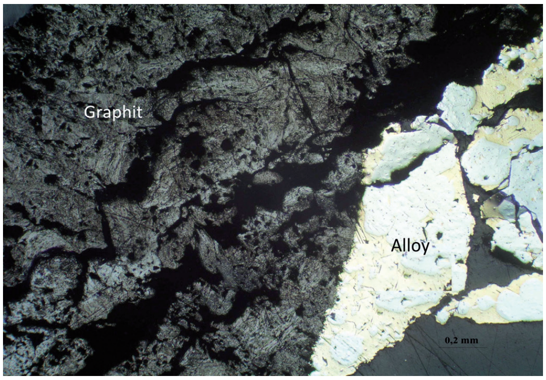

Fig. 2: *Micro-image of the slag produced by plasma melting.*

Fly ash was trapped in a cyclone separator located behind the reaction space in a plasma reactor where it was subsequently cooled to the temperature of approximately 160 °C. The chemical composition of such fly ash is summarised for both experiments in Table 5. The chemical analyses indicate that the fly ash contained mainly CaO, MgO, SiO_2 and Al_2O_3 oxides mechanically pulled down into the charge. The fly ash also contained the unreacted carbon and condensed vapours of Na, Ni, Co and Fe. Such fly ash may easily be recycled; this will increase the total recovery of metals.

Syngas (SG) produced during the melting process was purified as described in the experiments discussed in the literature [2]. Average concentrations

Table 2: *Basic data on the input materials for the process of ECaB melting.*

Experiment	*ECaB (kg)*	*Slag-forming additives (kg)*	*Reducing agent (kg)*	*Experiment duration (min)*	*El. energy consumption (kWh)*	*Plasma-forming gas consumption* $(l\cdot min^{-1})$
1	15	4.5	1.0	360	57.64	8.5
2	20	9.0	4.0	420	61.78	8.5

Table 3: *Chemical analyses and weights of alloys obtained in individual experiments.*

ALLOY		*Chemical composition (%)*					
Experiment	*FeCoNi alloy (kg)*	Fe	Ni	Co	Cr	Cu	Mn
1	3.67	60.06	13.78	15.25	7.35	1.14	2.39
2	5.61	45.70	6.82	29.51	3.32	12.86	1.66

Table 4: *Chemical analyses and weights of slags obtained by plasma melting.*

SLAG		*Chemical composition (%)*						
Experiment	*Slag (kg)*	CaO	SiO_2	MgO	Al_2O_3	Co	Fetotal	C
1	5.50	13.83	14.40	0.27	50.28	0.29	2.85	16.26
2	13.10	15.09	8.76	0.96	61.53	0.57	1.08	10.20

Table 5: *Chemical analyses and weights of fly ash.*

FLY ASH		*Chemical composition (%)*								
Experiment	***Fly ash (kg)***	CaO	MgO	SiO_2	Al_2O_3	Na	Ni	Co	C	Loss of annealing
1	2.00	16.20	0.71	12.62	8.90	18.77	0.36	0.44	18.35	22.73
2	3.50	17.47	0.69	10.18	11.62	22.75	0.58	0.57	10.83	24.30

Table 6: *Average values of syngas components obtained by continuous measurements during the process of plasma melting and gasification.*

SYNGAS		*Average chromatography analysis (vol. %)*				
Experiment	***Syngas ($m^3 \cdot h^{-1}$)***	H_2	CO	CO_2	CH_4	N_2
1	12.57	5.53	16.70	1.27	0.00	76.50
2	12.32	7.71	20.20	1.42	0.00	70.67

of the key syngas components identified by continuous chromatography measurements of CO, CO_2, H_2, N_2 and CH_4 are summarised in Table 6.

Figure 3 presents the composition of the syngas produced in Experiment 1. The presented data depend on the period during which electrochemical cells and batteries, slag-forming additives and the reducing material were added into the charge.

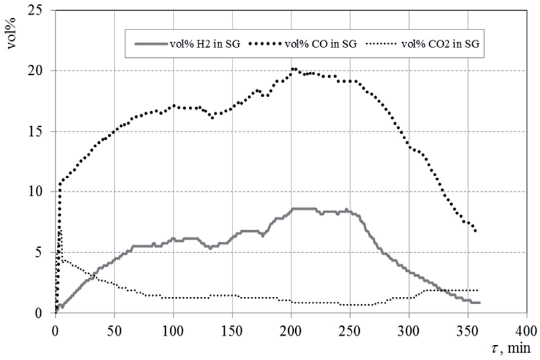

Fig. 3: *Syngas composition during the first experiment.*

The average LHV of SG for the entire period of Experiment 1 was 2.706 $MJ \cdot m^{-3}$. Purified SG was burned together with natural gas in a cogeneration unit with the CAPSTONE C65 micro-turbine where electric and thermal energies were produced. The cogeneration unit was operated with a present required electric power of 55 kW. The changes in the proportion of natural gas contained in the mixture burned during the experiment are shown in Fig. 4. The graph indicates that on average the syngas replaced 4.3 % of natural gas. During the syngas incineration, also CO, being the dominant component thereof, is liquidated.

The total recovery of the non-ferrous metal in question – ***cobalt*** into the metal phase was rather high. In Experiment 1, it was 94.59 %, and in Experiment 2 it was 95.76 %.

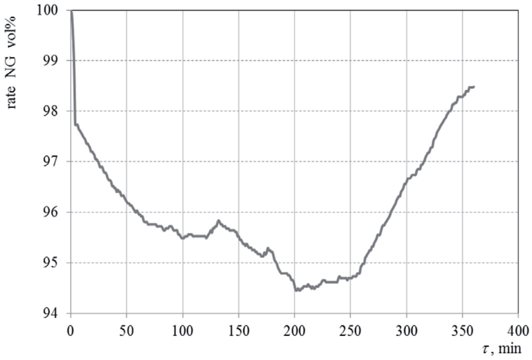

Fig. 4: *Rate of NG in the mixture with syngas during Experiment 1.*

4. Conclusion

The objective of the present article was to point out the possibility of high-temperature melting and recovery of decommissioned electrochemical cells and batteries. The secondary objective was to identify the recovery of cobalt into the metal phase and assess the energy gain from the utilisation of syngas within the total balance of the melting process.

During the experiment molten alloy, slag, fly ash and syngas were obtained. The molten Fe-Ni-Co alloy contained more than 15 % Co, which shows the high cobalt recovery rate. The total recovery of the non-ferrous metal in question – ***cobalt*** into the metal phase was approximately 95 %. The slag contained the concentrated elements with high affinity to oxygen, such as Al, Si, Mg and Ca, as well as Fe in form of FeO oxides. The loss of Co in the slag was very low. The LHV of the produced syngas is not very high with regard to its composition; it is approximately 3 MJ·m^{-3}. Nevertheless, in the operation of a micro-turbine, syngas may replace more than 4 % of natural gas. A disadvantage of simple pyrometallurgical processes is that all of the components of the waste are melted; however, extraction and separation of several elements may require complicated additional treatments [17]. The high temperature process is also more energy intensive compared to hydrometallurgical processes. Its environmental significance is justified only in preventing the waste storage with the aim of maximum recycling of the products obtained.

Acknowledgments

This article was prepared with the support from the grant projects VEGA no. 1/0108/19 and SP2019/74-FMT VŠB TUO.

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