

## Recovery of Metallic Lead from Lead Oxide Residues by Polyethylene Terephthalate

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The present article offers a new technology with the use of secondary polymer – polyethylene terephthalate (PET) for removing metallic lead from lead oxide residues instead of expensive traditional reducers (coke, natural gas, etc.). For this purpose, waste alcoholic and non-alcoholic beverage package bottles are used, their main component is PET. Polymer waste does not degrade for many years and, if exposed to nature, creates major environmental problems. This is why their proper disposal is very important to improve the ecological state of the environment. One of the aspects of our innovative technology is the use of potassium and sodium carbonate melt as a reaction medium in the lead oxidation recovery process instead of the traditional chloride system. As its melts, harmful products are released. Based on our study, it has been established that carbonate alloys, which perform the function of a flux, at the same time shield lead ions from oxygen and promote the adsorption of lead vapor droplets, thereby reducing the evaporation of lead and its compounds and their scattering in the environment what is important for the ecology. In lead oxide recovery processes using PET as the reducing agent, the recovery reactions take place at relatively lower temperatures (750-800°C) than in traditional technologies, resulting in increased metal lead yield. The quality of lead recovered during the experiments was checked by spectral analysis – Atomic Absorption Spectroscopy Method, according to which it can be said that high quality (98%) metal bullets are obtained. Thus, with the new technological method proposed by us, by joint processing of polymer tare and lead rust industrial and household waste, it is possible to obtain low-cost and high-quality metal lead. It is much safer in terms of environmental pollution and is more economical compared to traditional technologies. © 2022 Bull. Georg. Natl. Acad. Sci.

Lead, lead oxide, polyethylene terephthalate, carbonate smelts, recovery reactions

The rapid development of the world automotive industry has led to a significant growth trend in the production of lead-acid starter batteries. Lead and its alloys are also indispensable products for many

industries. Therefore, the demand for them is growing every year around the world.

Lead production with the processing of raw materials is associated with significant technical,

economic and environmental problems (one ton of lead requires about 1000 tons of ore processing). In the last decades, the lead content in ore has decreased by 20-50%, which makes the processing of new ores even more unprofitable.

Thus, due to the depletion of lead natural resources, its uptake into recycled raw materials is becoming increasingly relevant. Constant updating of motor batteries leads to the accumulation of lead and its compounds in the environment. Due to its high toxicity, lead scrap poses major environmental problems, necessitating the development of new, environmentally safe, innovative technologies to recycle lead.

Such a product is much more profitable due to low energy costs and other technological advantages: high lead content in raw materials, less conventional energy consumption per unit of finished product, relatively small volume of slag, dust and gases generated during processing, etc.

The major environmental problems are caused by polyethylene terephthalate waste used as packaging material and a carrier for alcohol and soft drinks, the number of which is constantly increases in the world, whose disposal is of great importance for improving the ecological condition of the environment. Currently only a small fraction of the residual polymers are recycled and returned to production.

The aim of the work was to develop a new technology for the production of metallic lead using secondary raw materials – lead oxide and polyethylene terephthalate obtained from batteries. This would make it possible to replace the expensive regenerative coke with cheap used PET, which would have a significant economic and environmental impact.

The available literature gives scarce data on the use of carbonates as fluxes in lead recovery technology are scarce. Their use is known at relatively low temperatures of 750-800°C [1].

One of the main problems in lead production is the lead transferred to the slag, which depends on

the solubility of lead oxide in the flux. As some data suggest, its concentration in the slag changes in the range 10-35% [2, 3].

In order to ascertain the amount of the lead recovered to the slag, we studied the solubility of lead oxide in the melt carbonates with different content at 750-800°C. The solubility of the lead oxide in the melt carbonates is also very important for the process stability and increasing lead output.

It is known from the literature that the solubility of oxides in general, including lead oxide, depends on both, the melting temperature and the melting composition [4, 5]. In particular, the concentrations of cations in the melt, which have a high charge density and which significantly change the base-acid properties of the melt, are of great importance [6]. Such ions include lithium (Li<sup>+</sup>), magnesium (Mg<sup>2+</sup>) and calcium (Ca<sup>2+</sup>).

The aim of the experiments was to determine the dependence of the solubility of lead oxide (PbO) on melting temperature and composition in double and triple carbonate alloys – K<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub>-CaCO<sub>3</sub> [7].

It is known that the melting temperatures of Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> of individual carbonates are 854°C and 891°C, respectively, while the decomposition temperatures are equal to 1000 and 1200°C. The decomposition temperature of CaCO<sub>3</sub> is relatively low: 840°C [8, 9].

Due to the fact that the melting temperature of the double and triple carbonates eutectic is 700-720°C, the working temperature was selected at 750-800°C. At this temperature, the evaporation of both carbonates and lead oxide is minimal and therefore the target product-metal lead losses are small [10].

## Experimental Section

The experiments were conducted in a shaft electric furnace with a quartz screen embedded. The screen had a refractory ceramic roof with three pipes in it: one to carry the weight of the lead, the other to react with the air, and the third to remove the exhaust

gases from the reaction area. The construction of the roof also allowed for visual observation of the slope.

The experiments were conducted under a special vent umbrella. The temperature in the reaction area was measured with a chromium-alumel thermocouple. Carbonate salts were decomposed in corundum pans.

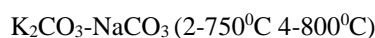
Carbonate salts in the amount of 50-50g each were used for  $K_2CO_3-Na_2CO_3$  smelting and 45-45-10g for  $Na_2CO_3-K_2CO_3-CaCO_3$  smelting for the experiment.

Accordingly, the weighed salts were loaded into corundum pans placed in a shaft furnace, where the temperature was 850°C. After melting the salts, the temperature was reduced to 750 or 800°C, depending on the terms of the experiment. The carbonate melt had lead oxide as one-gram weights. Following the delay of 20-25 minutes, the sample was taken for analysis.

To determine the solubility of lead recovered in melts of carbonate mixtures of different compositions, the analysis of solid powders obtained by atomic absolute spectroscopy was performed after cooling the melts, for which nitric acid solutions of medium samples (approximately 0.5 g) of these powders were pre-prepared. The analysis was performed on the tool Analyst 200 (PerkinElmer).

## Results and Discussion

The experimental results are given in Fig.



The Fig. shows that the solubility of lead oxide in the flood of K and Ca at 750°C is maximum 8%, and no more than 5% in  $K_2CO_3-Na_2CO_3-CaCO_3$ . As it was expected at 800°C, these numbers grow insignificantly.

Decreased solubility of lead oxide in the addition of calcium carbonate to alkali metal alloys may be explained by complex physicochemical processes due to the high specific charge density of calcium ions compared with potassium and sodium ions [11]. Lead ion is likely to be bound by calcium ( $Ca^{2+}$ ) ions at the expense of the formation of various compounds. Such may be calcium seals  $Ca [(PbCO_3)]$ ,  $Ca_2 [(PbCO_3)]_2$ , it is possible to form other mixed complexes, the solubility of which differs from the solubility of lead oxide [12]. Thermal decomposition of calcium carbonate also produces calcium rust with a melting point of 2880°C and poorly soluble carbonate melt. The production of these substances significantly increases the melting temperature of flux, which is undesirable for the stability of the low-temperature lead recovery process.

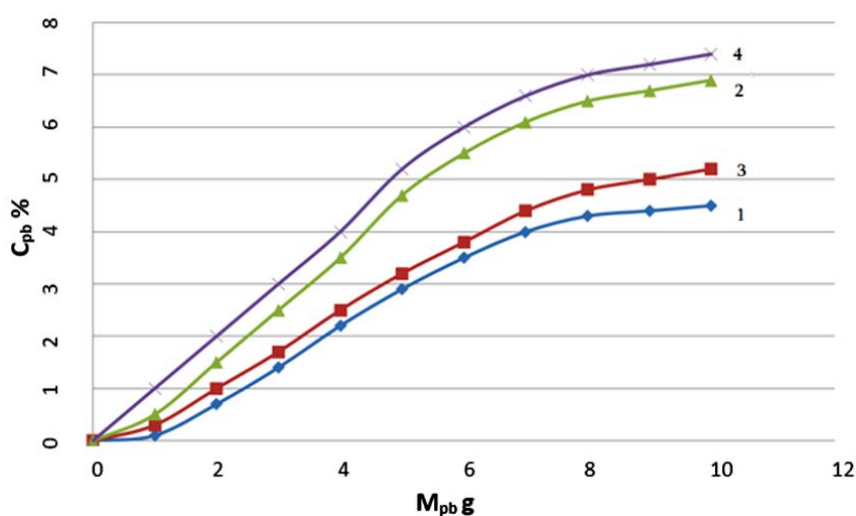


Fig. Dependence of the lead oxide solubility on the temperature and melting composition ( $M_{PbO} = 100$  g).

It is known that in case of lead oxide reduction by coke, it is pre-thermally sintered so that the reducing gases (CO, H<sub>2</sub>) generated during coke combustion can easily penetrate between the lead oxide granules and achieve a high recovery rate.

Instead of reducing lead oxide with coke, we used secondary polymer polyethylene terephthalate in the experiments, and instead of sintering lead oxide, it was briquetted with its polyethylene terephthalate, for the following reasons:

1) Lead oxide is briquetted at low temperature (200-240°C), under minimum pressure and therefore, energy consumption is negligible in terms of unit output;

2) The lead oxide and bonding polymer in the briquette are distributed homogeneously, which leads to a high probability of contact of the

regenerating and regenerated metal during the technological process;

3) The regenerating gases and air generated during the technological process will pass smoothly between the briquettes, which leads to a high percentage of lead recovery.

To achieve a homogeneous distribution of the reducing agent and lead oxide in the briquette, a polymer shredding technology has been developed, which involves pre-thawing the polymer at 270°C, mechanical grinding and separation. Briquetting was done by means of hydraulic pressure.

The briquettes, in which the concentration of polyethylene terephthalate varied from 5 to 50%, were prepared to select the optimal concentrations of the reducing and reduced metal oxide. Lead oxide was also recovered in the shaft furnace.

**Table 1. Recovering of the lead oxide by PET. The weight of briquette M=200 gr; T=750°C**

Sample N	Content of PETP. %	Content of Lead in the oxide briquette. %	Content of Lead in the briquette. %	Weight of metallic lead. gr.	Output of the lead. %
1	10	90	25,06	21,18	87,8
2	15	85	23,67	21,35	90,2
3	20	80	22,27	21,54	94,9
4	25	75	20,88	19,85	95,1
5	30	70	19,49	18,51	95,0
6	35	65	18,09	17,18	95,0
7	40	60	16,70	15,41	92,3
8	45	55	15,30	13,94	91,1
9	50	50	13,92	12,53	90,0

**Table 2. Lead oxide content in lead slag after recovery of the oxide with polyethylene PET in the melt K<sub>2</sub>CO<sub>3</sub> - Na<sub>2</sub>CO<sub>3</sub>, M=200 g, T=750°C**

Sample №	Content of Lead oxide in the briquette. %	Content of PETP. %	Content of Lead oxide in the briquette. %.	Weight of slag. gr.
1	10	90	3,41	190
2	15	85	3,18	189
3	20	80	2,25	192
4	25	75	1,98	191
5	30	70	2,00	188
6	35	65	1,95	185
7	40	60	1,95	186
8	45	55	1,8	185
9	50	50	1,7	183

To recover the lead, the briquettes were placed in carbonates permeated in a corundum tub and air was blown through a compressor. The recovery process lasted for 15-20 minutes, then the corundum crucible was removed from the furnace and cooled, and the recovered lead was separated from the flue. The obtained lead samples were analyzed to determine the quality of the lead. The results of the experiments are given in Table 1.

As Table 1 shows, the ratio of reducing and reduced lead oxide varies within a wide range, although the optimal ratio is 25% polyethylene terephthalate and 75% lead oxide. The percentage yield of lead was reduced at lower or higher concentrations of regenerative polyethylene terephthalate. The reason for this is the lack of a restorer in the first case, and the excess of a restorer in the second case. As the combustion duration and temperature increase, the evaporation rate of lead oxide, metallic lead, and flux increases, and the yield of the resulting product - the reduced lead decreases.

Following the experiments, the flux was weighed and analyzed to determine the amount of evaporated salts and the concentration of lead oxide dissolved in the flux, the results of which are given in Table 2.

As Table 1 shows, the content of the lead oxide in the slag following the reduction of oxide with polyethylene terephthalate, the percentage is the lowest in case of the following ratio of the reducing and the reduced lead oxide: 25% polyethylene terephthalate and 75% lead oxide, which also has the highest lead yield.

During the experiments, the quality of the recovered lead was checked by spectral analysis using the method of atomic absorption spectroscopy, according to which, it can be said that the quality of the recovered lead is quite high and the percentage of pure lead in it is 97.01% to 97.9% what is quite high.

The experiments have confirmed the possibility of using carbonate alloys both individually and in a

mixed form to reduce lead oxide, although potassium and sodium carbonate alloys should be used in flux to conduct the process at relatively low temperatures (750-800°C). Carbonate smelting, which performs the function of flux, at the same time shields lead ions from oxygen, reduces the evaporation of lead and its compounds, which is important both, for improving the environmental condition and for the health of production personnel.

## Conclusions

The studies have shown that the use of polyethylene terephthalate, as a reducing agent in the absence of metallic lead, has a number of advantages over coke recovery:

- 1) Lead dioxide in other known technologies must be converted into granules prior to the recovery so that the carbon dioxide obtained by burning coke can easily penetrate between the granules (fragments). The yield of metallic lead does not even exceed 85-87%; in our case, permeable polyethylene terephthalate is used to briquette lead dioxide, which is in a direct contact and is evenly distributed between the lead dioxide particles, which ensures maximum contact of the gases released during the combustion of the reducing reagent with the lead oxide particles, thus increasing the lead output (92-95% of the theoretical output).

- 2) The recovery temperature of lead with coke ranges within 1100-1200°C, which leads to intensive evaporation of lead oxide and metallic lead, causes environmental pollution, and the process is less profitable economically. The operating temperature of our experiments did not exceed 800-850°C, which leads to less evaporation of lead and its compounds, and the technology is both more environmentally friendly and economically more profitable than traditional technologies;

- 3) When recycling lead by traditional methods, flux waste containing 8-10% lead is obtained,

which is difficult to recycle, and the vaporized and filtered lead compounds are almost never used for recycling, creating even more significant environmental problems;

The use of flux carbonates to recover lead, if lead and its compounds are trapped, will make it possible to re-briquette them with the permeable regenerator and return them to production, which will further reduce lead and carbonate losses while

the technology becomes environmentally safe and economically viable.

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### ელექტროქიმია

## ტყვიის ოქსიდის ნარჩენებიდან მეტალური ტყვიის აღდგენა პოლიეთილენტერაფტალატის საშუალებით

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(წარმოდგენილია აკადემიის წევრის თ. ნატრიაშვილის მიერ)

სტატიაში შემოთავაზებულია ტყვიის ჟანგისგან მეტალური ტყვიის აღდგენის ახალი მეთოდი მეორადი პოლიეთილენტერაფტალატის საშუალებით ძვირადღირებული ტრადიციული აღმდგენლების (კოქსი, ბუნებრივი აირი) მაგივრად. ამ მიზნით გამოყენებულია უალკოჰოლო და ალკოჰოლიანი სასმელების ნარჩენი ტარა ბოთლების სახით, რომლის პირითადად შემადგენელ კომპონენტს წარმოადგენს პოლიეთილენტერაფტალატი (პეტფ). ჩვენი ინოვაციური ტექნოლოგიის ერთ-ერთ ასპექტს წარმოადგენს ტყვიის ჟანგის აღდგენის პროცესში სარეაქციო გარემოდ კალიუმისა და ნატრიუმის კარბონატების ნალღობის გამოყენება ნაცვლად ტრადიციული ქლორიდული სისტემისა, რომელთა ლღობის შემდეგ ჯანმრთელობისთვის მავნე პროდუქტები გამოიყოფა. ჩვენ მიერ ჩატარებული კვლევების საფუძველზე დადგენილია, რომ კარბონატული ნალღობი, ასრულებს რა ფლუსის ფუნქციას, ამავდროულად, ახდენს ტყვიის იონების ეკრანირებას ჟანგბადისაგან და ხელს უწყობს ტყვიის ორთქლის წვეთებად შეწებებას, რის შედეგადაც მცირდება ტყვიისა და მისი ნაერთების აორთქლება და გარემოში გაბნევა., რაც

მნიშვნელოვანია გარემოს ეკოლოგიური მდგომარეობის გაუმჯობესებისათვის. ტყვიის ოქსიდის აღდგენით პროცესებში პოლიეთილენტერაფტალატის, როგორც აღმდგენი აგენტის გამოყენებისას აღდგენის რეაქციები მიმდინარეობს შედარებით დაბალ ტემპერატურებზე (750-800°C), ვიდრე აქამდე არსებულ ტრადიციულ ტექნოლოგიებისას, რის შედეგადაც იზრდება მეტალური ტყვიის გამოსავალი. ექსპერიმენტების დროს აღდგენილი ტყვიის ხარისხის შემოწმება ხდებოდა სპექტრალური ანალიზით – ატომურ აბსორციული სპექტროსკოპიის მეთოდით, რომლის მიხედვითაც შეიძლება ითქვას, რომ მიიღება მაღალი ხარისხის (98%) მეტალური ტყვია. ამრიგად, ჩვენ მიერ შემოთავაზებული ახალი ტექნოლოგიური მეთოდით – პოლიმერული ტარისა და ტყვიის ჟანგის საწარმოო და საყოფაცხოვრებო ნარჩენების ერთობლივი გადამუშავებით შესაძლებელია დაბალი თვითღირებულებისა და მაღალი ხარისხის მეტალური ტყვიის მიღება. იგი გაცილებით უსაფრთხოა გარემოს დაბინძურების თვალსაზრისით და ტრადიციულ ტექნოლოგიებთან შედარებით უფრო ეკონომიურია.

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