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WASTES FROM THE COAL-ENRICHMENT PROCESS AS ALTERNATIVE REDUCERS FOR LEAD SMELTING FROM LEAD-ACID ACCMULATOR SCRAP

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In the paper, results of the study on a possible utilization of coal-enrichment wastes as alternative reducers for lead smelting from acid-lead accumulator scrap are presented. For the experiments, the following alternative carboniferous reducers were selected: coal slurry, anthracite dust and coal soot. The investigations included both laboratory-scale experiments and semi-industrial tests in a rotary furnace. The findings allowed for a review of the effects of a sample type (loose material or material post a preliminary agglomeration process), loaded into the furnace, on a final process yield.

Keywords: coal wastes, reduction, lead, accumulator scrap, waste recycling

INTRODUCTION

For many years, disadvantageous reduction in natural resources, whose usage is economically justified, has been observed. These materials include metal ores and energy resources. To prevent their reduction, there is increasing interest in metal secondary raw materials and alternative carboniferous materials. At present, there are higher amounts of some metals obtained from secondary materials (scraps) than those produced from primary ones (metal ores). The examples are aluminium and lead. In the case of coal energy resources, fine-grained wastes generated during coal enrichment processes or coke production are of a higher economic importance.

The post-coal enrichment wastes show a large variety of chemical compositions, which is demonstrated in Table 1 where chemical data regarding flotation tailings are presented [1].

It should be noted that the amounts of these wastes in Poland are difficult to determine, particularly for slurries and tailings, which is mainly due to the fact that, practically, only current production waste and waste collected in sedimentation tanks are subject to a production balance. Thus, depending on their generation period, clear differences with respect to their calorific values are very frequently observed [2]. The caloric values of over 60 % of these materials are above 10 MJ/kg, while only 10 % – above 15 MJ/kg.

Table 1 **Chemical compositions of flotation tailings**

Component	Content limits / %mass	Average content / %mass
SiO_2	34,66-66,91	49,33
Al_2O_3	13,34-26,50	21,64
TiO_2	0,83-1,96	1,31
Fe_2O_3	0,91-12,90	5,48
CaO	0,06-4,68	0,93
MgO	0,30-4.33	1,32
K_2O+Na_2O	1,07-4,33	2,52
Sc	0,97-3,98	1,82
C	8,87-30,50	20,55

Currently, coal-enrichment wastes are mainly used as components of coal blends and concentrates, as a material for co-production of special fuels or as fuel alone. There are increasingly frequent attempts to apply these materials in other industries as substitutes for coke and coal used in their technologies [3 - 6], i.e. in metallurgical processes in which metals from both processed and secondary materials are used [7, 8]. In the paper, results of the study on utilization of coal slurries as fly ash substitutes in the treatment of lead-acid accumulator scrap are presented. For comparison, anthracite dust and coal soot were used as alternative reducers.

MATERIALS

In the process, coal slurry, anthracite dust and coal soot were used as fly ash substitutes. Their characteristics are presented in Table 2.

As plumbiferous material, metalliferous sludge from lead-acid accumulator scrap was utilized. Its chemical composition is presented in Table 3.

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Table 2 **Basic parameters of carboniferous raw materials used in the study**

Parameters of the applied reducer	Coal slurry	Coal soot	Anthracite dust
Calorific value / MJ/kg	22,4	22,4-33,0	20,3
Ash content / %mass	10	3,8-22,2	24,1
Humidity / %mass	18,3	5-73,8	3,5
Sulphur content / %mass	0,4	0,32	0,99
Volatile matter / %mass	22,5	8-19	5,3

In the investigated material, lead occurred in the metallic phase as well as in the form of $PbSO_4$, $PbO \cdot PbSO_4$, $2\ PbO \cdot PbSO_4$, $4\ PbO \cdot PbSO_4$, PbO and PbS.

As additives for the tests, sodium carbonate and iron chips were used – a lead desulphurisation agent and a lead sulphide reducer, respectively.

Table 3 **Chemical composition of plumbiferous sludge**

Element	Content / %mass
Pb	75,600
Cd	0,003
Fe	0,450
Hg	0,1 ppm
Mn	0,010
C	2,110
S	3,650
Sb	0,170
Zn	0,020
Water content	8,700

RESULTS

The investigations of plumbiferous materials were performed in three series. In the first series, mixed charge materials were loaded into a crucible in the form of loose material, while in the second one, the materials were previously subjected to a preliminary agglomeration process: granulating or briquetting. In the third series, semi-technical scale tests were performed with the use of agglomerates selected based on the results of Series 1 and 2. All Series 1 and 2 experiments were conducted in an electrical furnace. Basic parameters of the experiments are listed in Table 4.

Table 4 **Basic parameters of the laboratory tests**

Process parameter	Min value	Max value
Process temperature / °C	1 150	1 200
Reducer additive / %mass	5	30
Charge material additives / %mass	5	10
Smelting duration / h	2	3

Lead smelting semi-technical tests were carried out in a rotary furnace equipped with a steel retort for charge material loading and blending. In the furnace working chamber, a natural gas burner was installed. A schematic diagram of the furnace is presented in Figure 1. After each experiment, the obtained metal and slag fractions were weighed and chemically analysed.

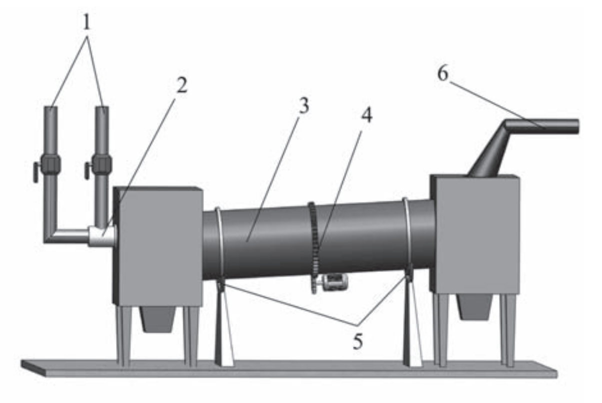

Figure 1 A schematic diagram of a laboratory roll-down furnace used for investigations. 1 – natural gas and air supply; 2 – a burner; 3 – a rotary furnace; 4 – a furnace drive system; 5 – rollers for rotary motion; 6 – gases outlet

The charge material for investigations performed in the rotary furnace was agglomerate containing plumbiferous sludge as well as anthracite dust (6 %), steel filings (8 %) and hydrated lime (5 %). The lead content in the blend was 59,5 % mass.

In Table 5, sample results of lead smelting from the loose material are presented, while Table 6 lists results of its smelting from the post-agglomeration charge material. Graphic interpretations of the results are shown in Figures 2 – 5.

Table 5 **Results of plumbiferous material remelting with the use of technological additives – loose charge material**

No	Temp. / K	Time / h	Charge material additives / %mass				Average lead yield / %
			C*		Fe	Na_2CO_3	
1	1 423	2	5	S	5	10	39,3
2			10	So	10	5	59,1
3			10	D	5	5	50,6
4		3	5	S	5	10	42,7
5			10	So	10	5	60,2
6			10	D	5	5	52,7
7	1 473	2	5	S	5	10	47,1
8			10	So	10	5	64,7
9			10	D	5	5	55,9
10		3	5	S	5	10	44,9
11			10	So	10	5	67,1
12			10	D	5	5	56,3

*Where: S – coal slurry; So – coal soot; D – anthracite dust.

The letter G refers to the tests with the use of granulated material; the letter B is related to the tests with the use of briquetted material.

SUMMARY

The results of lead sludge remelting based on the treatment of acid-lead accumulator scrap with fine-grained carboniferous waste materials (coal slurry, anthracite dust, coal soot) indicate a potential for their al-

Table 6 **Results of plumbiferous material remelting with the use of technological additives – post-agglomeration charge material (in all examined samples the content of Fe was on a constant level – 10 % mass)**

No.	Temp. / K	Time / h	Charge material additives, / %mass			Mass of the metallic fraction after remelting, / g	Pb yield / %
			C*		Na_2CO_3		
B1	1 473	2	10	S	5	299,4	79,2
B2			10	So	5	356,1	94,2
B3			10	D	5	333,0	88,1
B4	1 423	2	10	S	10	290,7	76,9
B5			10	So	10	365,9	96,8
B6			10	D	10	328,1	86,8
B7	1 473	3	8	S	10	303,2	80,2
B8			8	So	10	344,4	91,1
B9			8	D	10	356,8	94,4
G1	1 473	2	10	S	5	343,6	90,9
G2			10	So	5	367,4	97,7
G3			10	D	5	336,8	89,1
G4	1 423	2	10	S	10	335,3	88,7
G5			10	So	10	341,3	90,3
G6			10	D	10	347,0	91,8
G7	1 473	3	8	S	10	337,6	89,3
G8			8	So	10	362,1	95,8
G9			8	D	10	345,5	91,4

* Where: S – coal slurry; So – coal soot; D – anthracite dust.

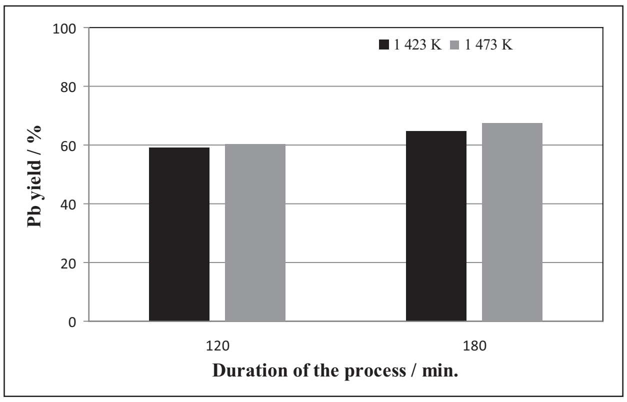

Figure 2 Lead yield for the process of loose material remelting (additives: 10 % coal soot, 10 % Fe, 5 % Na_2CO_3)

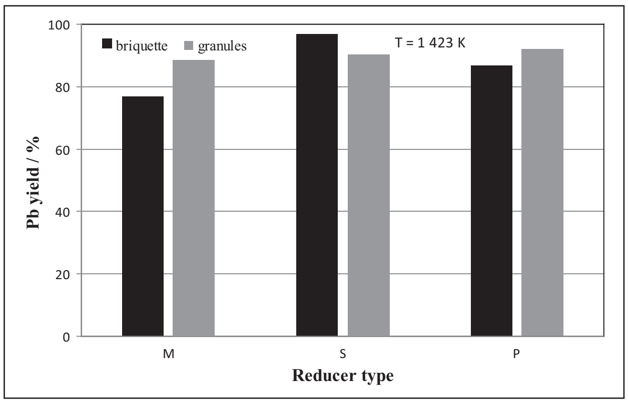

Figure 3 Lead yield for the process of post-agglomeration material remelting (additives: 10 % C; S – coal slurry; So – coal soot; D – anthracite dust; 10 % Fe, 10 % Na_2CO_3, duration of the process: 120 min)

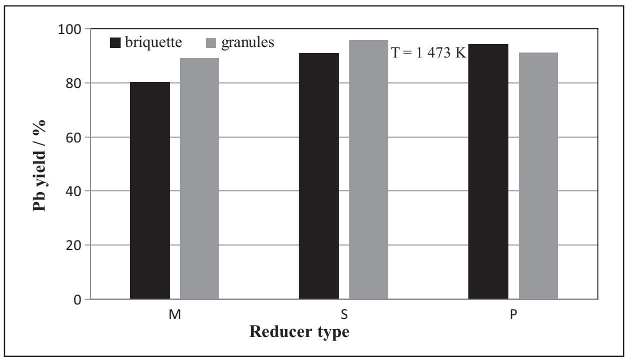

Figure 4 Lead yield for the process of post-agglomeration material remelting (additives: 8 % C; S – coal slurry; So – coal soot; D – anthracite dust; 10 % Fe, 10 % Na_2CO_3, duration of the process: 180 min)

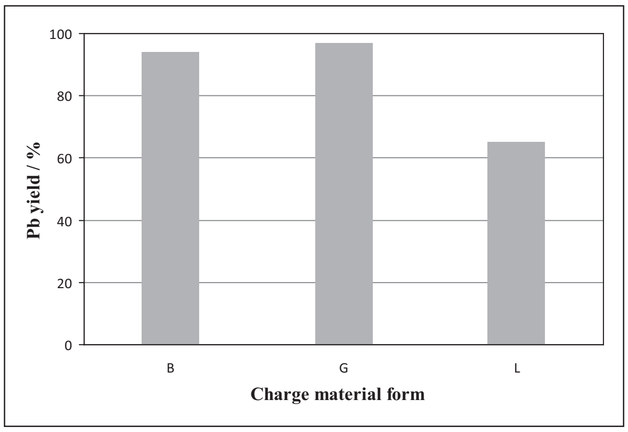

Figure 5 Lead yield for the process of remelting of plumbiferous materials obtained from the treatment of acid-lead accumulators with addition of 10 % mass reducer (coal soot), 10 % mass Fe, 5 % mass Na_2CO_3. The process temperature: 1 473 K, duration: 120 min. The letters denote, respectively: B – briquetted material; G – granulated material; L – loose material loaded into the crucible

ternative application as fly ash substitutes. Efficiency of the reduction process is clearly related to the type of charge material. A high lead yield (over 90 %) was obtained in the remelting tests with charge material that was previously subjected to the preliminary agglomeration process. Lead smelting with the use of loose material yields up to 65 % of the metal.

In semi-technical tests performed in the rotary furnace, the maximum lead yield was 82 %. It should be assumed that the lead yield below 90 % in the semi-technical tests may be affected by two factors. The first factor is related to the physicochemical properties of granulated material which, following a longer seasoning period, shows higher plasticity. This means a considerable fraction of the material that adhered to the furnace surface and remained unreacted. Secondly, the furnace design allows for filling it at one end at an angle to the horizontal axis, which led to a faster transfer of some material along the furnace axis.

The results of laboratory and semi-technical tests allow for the assumption that the proposed, alternative fine-grained coal materials and the way of their preparation may be utilized on the industrial scale for processing the metalliferous fraction based on the acid-lead accumulator scrap treatment.

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