LEAD-BASED WASTES FROM METALWORKING PROCESSES – THE POSSIBILITY OF USING

Jitka MALCHARCZIKOVÁ, Simona TURKOVÁ

VSB - Technical University of Ostrava, Ostrava, Czech Republic, EU, jitka.malcharczikova@vsb.cz, simona.turkova.st@vsb.cz

https://doi.org/10.37904/metal.2024.4970

Abstract

The paper characterizes selected lead-based wastes occurring in the metalworking industry, such as wire manufacturers using lead baths in the heat treatment process. Attention is focused on the possibility of using the proportion of lead in direct metal form, which can occur in certain types of waste. For waste, the content of selected metals and the form of their occurrence was determined. For waste with lead in metallic form, pyrometallurgical tests were performed to obtain the proportion of lead from industrial waste. Subsequently, the purity of the obtained product was determined, which is related to its use directly back into the given technological procedure. It was found, that with remelting of the given type of waste at relatively low temperatures it is possible to obtain an interesting proportion of pure lead. The secondary lead has sufficient purity and can be reused and thus support the sustainability of the process. Conversely, certain parts of waste contain such a small amount of metals, including lead, that it would be possible to use them in a different way than to pass them into the system as waste containing heavy metals. These wastes must then be recycled in specialized plants. Companies are currently reassessing their established procedures for dealing with production waste and looking for new possibilities for using waste directly in their plants. Recovering the share of lead in the process and the subsequent possibility of reassessment of the dangerousness of certain shares of industrial waste is a way to improve the company's position in waste management and the use of raw materials.

Keywords: Waste with lead, metals recovery, secondary lead, heavy metals, sustainability

1. INTRODUCTION

Lead is toxic and there is an effort to replace it in many applications [1]. However, there are applications in which it is still used. Many types of metal and metal-bearing waste with different proportions of lead are produced from the processes of using Pb. Lead can be in the form of metal or in the form of compounds in waste [2-4]. The issue of the processing and utilization of waste originating both from the production of lead or from the recycling of Pb waste, as well as from other production and processing processes is still being resolved [5-7]. Waste containing lead in various forms is also produced in the metalworking industry, e.g. during the wire drawing process, when during continuous (in-line) annealing of low carbon wire or patenting are used lead baths for thermal treatment of wires. Floating protective layers and tank covers on the surface of the lead baths are used to minimize heat losses, oxidation of lead and reduce emissions to air [8]. The surfaces of the liquid Pb baths are covered with covering layers based on anthracite or perlite, which are periodically changed. A large amount of hazardous waste is thus created. Businesses have to deal with this waste. After certain treatment of waste, the share of returnable waste can be increased, some less dangerous components can be separated and thus the share of hazardous waste processed in specialized recycling plants can be reduced. Pb from metal-bearing wastes can be generated by continuous annealing about 1-15 kg/t and by patenting 1-10 kg/t Pb wastes per ton of processed wire [8, 9]. Producers such as wireworks and air rifle cartridges producers can produce 25-29 t of waste with Pb per year, large producers up to 81 t (data from the Integrated Pollution Register for the Czech Republic for the year 2022) [10]. This idea falls into the area of the circular economy. Sustainability in the use of metals is becoming more important with regard to the decreasing availability of metals, especially for some countries. High-tech recycling technologies in the EU enable the recovery of common and valuable metals such as lead, tin, precious metals and other metals from e-waste, catalytic converters and other end-of-life products [11-12]. The direct processing of production and processing waste takes precedence and guarantees the minimization of waste generation.

2. DESCRIPTION OF THE EXPERIMENT

The waste from the heat treatment process of wires, in which a lead bath was used, was selected for the experiment. These were protective covering layers after regular periodic cleaning, which were assumed to contain a higher proportion of lead, but also of other metals from the processed material. Taking into account the visible occurrence of several size fractions in the samples, the samples were sieved to certain fractions. An indicative determination of the contents of selected metals was carried out as their average content and also in individual sample fractions. The samples were remelted in order to obtain the metallic fraction and to separate any fractions that could be separated from the industrial hazardous waste management system.

2.1. Preparation of the experiment

A sample of anthracite-based waste, which was used as a protective layer of a lead bath in the heat treatment of steel wires, was used for the experiment. The sample was separated into size fractions - coarse above 5 mm, medium and fine fraction below 0.4 mm. This waste includes lead in metallic form too. For samples the content of selected elements was observed by ED-XRF spectrometry. The determined values of the average waste composition and individual fractions are shown in **Table 1**. The measurement of the chemical composition is only indicative and is used to compare input and output parameters. The waste contains a significant proportion of lead and iron is also present. Other selected metals were contained in small amounts. The highest proportion of lead contained medium metal fraction with a size of 5-0.4 mm. Coarse fraction with a size up 5 mm contained only small amounts of metals. This fraction cannot just be pre-sieved, as there may be larger pieces of lead taken off which would remain in this fraction.

Table 1 ED-XRF analysis of Pb waste material – input for experiment (The values highlighted in grey are given in wt.ppm)

Sample	Content of metals (wt% / wt.pm)					Characterization of sample, sample fractions
	Mn	**Fe**	**Ni**	**Zn**	**Pb**	
1	1150 ± 93	12.04 ± 0.84	52 ± 13	4120 ± 606	35.10± 0.12	Input sample – average composition
2	1186 ± 23	11.78 ± 0.91	63 ± 3	3805 ± 412	37.08 ± 2.16	Input sample – average composition
3	35 ± 12	5560 ±1413	10 ± 3	2408 ± 2660	2879 ± 1434	Coarse fraction with a size up 5 mm
4	737 ± 74	6.06 ± 0.25	57 ± 20	1034 ± 702	44.85 ± 0.86	Medium metal fraction with a size of 5-0.4 mm
5	1435 ± 64	15.27 ± 1.25	76 ± 15	4315 ± 673	36.62 ± 0.74	Fine fraction below 0.4 mm
6	626 ± 222	5.90± 1.53	-	515 ± 176	35.60 ± 2.99	Pieces of metallic lead from the sample

Lead waste from the metalworking industry is in the **Figure 1**, on the left is a detail of the sample that was used for the experiment. It is evident that the waste was composed of several fractions and that it contained a metallic portion (graphite and metallic part of waste).

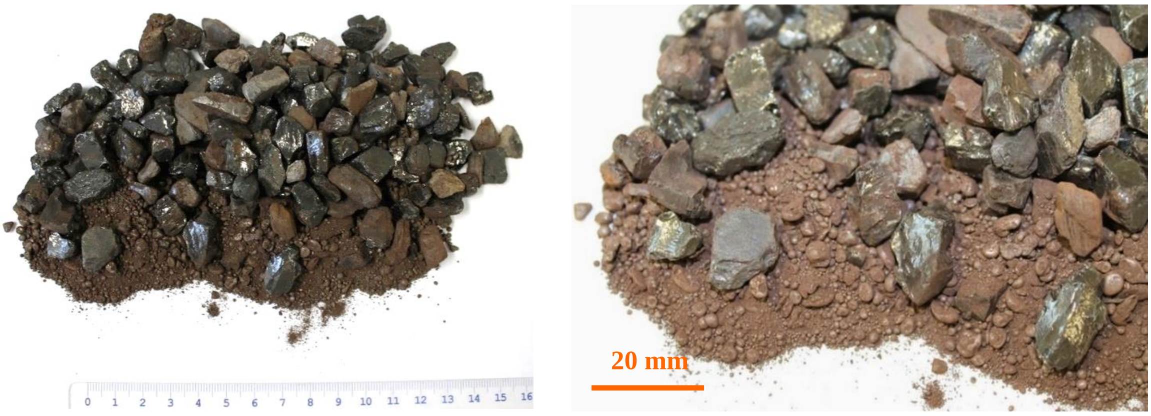

Figure 1 Lead waste from the metalworking industry

2.2. Pyrometallurgical process of metals recovery

The basis of further experiments was the pyrometallurgical processing of waste with the aim of obtaining a proportion of pure Pb, verifying the composition of the obtained products and the possibility of their use for the given application.

Melting was performed in an electric resistance furnace without a protective atmosphere. Waste was remelted at 500 and 450 °C in graphite crucible and mixing during process, time was 30 or 60 minutes. The lead melt was cast into a graphite mold. Size fractions from the residue after remelting were separated by sieving. The metal content in the waste and products (castings and separated fractions) were observed by ED-XRF spectrometry. The determined values are shown in **Table 2**. The melting product and the fractions obtained after sieving are shown in **Figures 3** and **4**. In **Figure 3** are castings of secondary lead (left) and coarse fraction (right), in **Figure 4** are fine fraction (left) and metallic part (right).

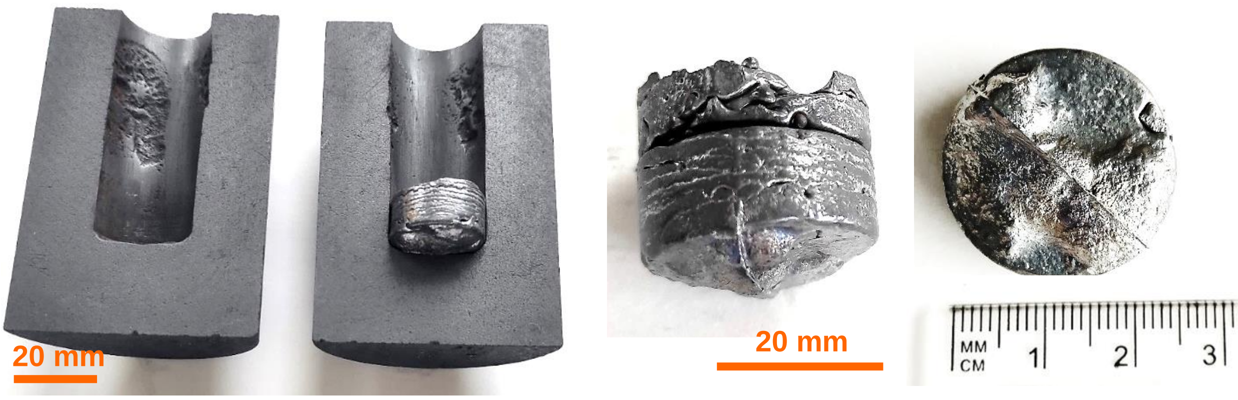

Figure 2 Graphite mould with lead (left), castings of secondary lead (right)

It follows from **Table 2** that it is very appropriate to sort the material into the size fractions. The coarse fraction does not contain significant proportions of metals and the composition is shown in **Table 1**. The determined lead content is still high in the fine and coarse fraction. It is believed that the fine fraction contains lead and iron compounds, mainly oxides. This fraction after separation should be processed in specialized recycling plants for the treatment of Pb waste. The metallic fraction should be returned to the waste remelting process. It is assumed that when processing larger portions of waste, this fraction would not be so significant and the transition of the metallic portion of lead from the waste to the melt would be more efficient. The secondary lead product obtained has a sufficient purity of 99.8-99.9 wt% and quality as shown in **Table 2** and **Figure 3**. A lower iron content in the recoverable proportion of secondary lead for the given application is not a problem. When processing waste on a larger scale, the quality of the Pb product is not expected to deteriorate, rather the opposite.

Table 2 EDX-RF analysis of products after Pb waste remelting **(**The values highlighted in grey are given in ppm)

Sample	Pb casting, fraction	Content of element (wt% / ppm)					Experimental conditions
		Mn	Fe	Ni	Zn	Pb	
M1	Metallic f.	709 ± 87	5.96 ± 0.32	42 ± 2	1131 ± 84	44.80 ± 2.72	Temperature 500 °C, time 30 minutes
	Fine f.	1119 ± 103	11.99 ± 0.59	58 ± 11	3421 ± 232	44.43 ± 0.40	
	Pb casting	0.015 ± 0.026	0.08 ± 0.07	-	-	99.91 ± 0.06	
M2	Metallic f.	732 ± 38	6.67 ± 0.26	59 ± 0	1085 ± 112	48.34 ± 0.81	Temperature 500 °C, time 60 minutes
	Fine f.	1082 ± 35	11.03 ± 0.97	48 ± 7	2939 ± 281	43.08 ± 1.88	
	Pb casting	-	0.17 ± 0.12	-	-	99.83 ± 0.12	
M3	Metallic f.	728 ± 18	6.37 ± 0.22	12 ± 17	1491 ± 61	46.82 ± 2.17	Temperature 450 °C, time 30 minutes
	Fine f.	1194 ± 141	12.58 ± 0.58	50 ± 9	3457 ± 401	40.96 ± 1.18	
	Pb casting	-	0.13 ± 0.02	-	-	99.89 ± 0.04	

Figure 3 Castings of secondary lead (left), coarse fraction (right)

Figure 4 Fine fraction (left), metallic part (right)

2.3. Possibilities of waste processing and utilization

A large amount of waste of this type is generated in a given operation and is generated periodically in certain periods. It is hazardous waste, where its handling is subject to special regulations. Solving the use of a certain proportion of this waste with a higher lead content directly in the plant environment is a partial goal of this work. This idea of reusing the share of lead obtained from waste, preferably directly for the original application, is in line with the idea of a circular economy and the introduction of low-waste technologies. Therefore, if it was possible to use part of the waste under acceptable economic and technological conditions, it would be possible to reduce the production of hazardous production waste in the plant, reduce the proportion of transported hazardous waste, reuse the proportion of Pb as a secondary raw material and also reduce the economic demands of the heat treatment process. Proposal for the processing of lead waste from the metalworking industry is in **Figure 5**.

From the values shown in **Table 2**, it follows that by means of the remelting of Pb waste, a proportion of very pure lead can be obtained, which should be reusable. The castings show a small proportion of Fe, however this should not be problematic for the given application. In addition, the iron can only be on the surface of the casting, and the overall purity of the product can then be higher. Thanks to the experiment, it was found that it is possible to obtain a valuable share of metallic lead usable as a secondary raw material from the given type of waste and thus partially ensure the circulation of the material in the given operation. The waste remelting temperature is not too high, the demands on the equipment would not be high, the operation is adapted to work with molten lead. In this way, it is possible to reduce the share of production waste and the production of hazardous waste. It would also be possible to obtain another proportion of Pb from the bulk metallic fractions, which would be appropriate to further verify.

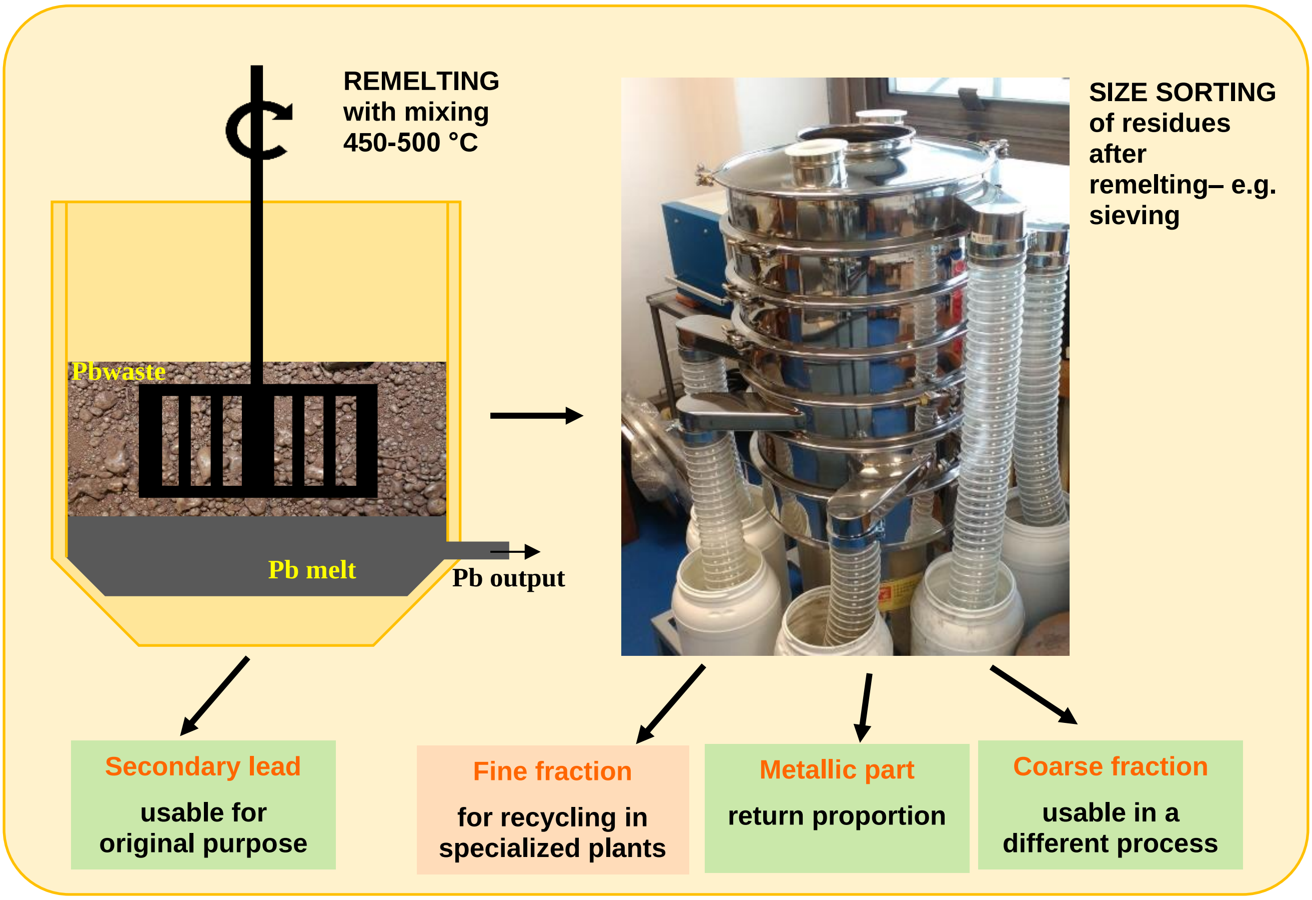

Figure 5 Proposal for the processing of lead waste from the metalworking industry

3. CONCLUSION

For the experiment waste from lead bath cover layers used for heat treatment of wires was used. This waste includes lead in metallic form too. Waste was remelted at 500 and 450 °C in graphite crucible. The lead melting was cast into a graphite mold. Size fractions from the residue after remelting were separated by sieving. The metal content in the waste and products (castings and separated fractions) was observed by ED-XRF spectrometry. It was found, that with remelting of the given type of waste at relatively low temperatures it is possible to obtain an interesting proportion of pure lead. After remelting the waste, secondary lead with a minimum content of 99.8 wt% was obtained. The coarse fraction does not contain a significant proportion of lead and other metals, it can be used for other processes. The procedure is applicable only for a certain type of waste with a proportion of metallic lead.

ACKNOWLEDGEMENTS

This article was created with the contribution of the Student grant competition project SP2024/062 „Influence of production, processing parameters and degradation mechanisms on the resulting material properties and lifetime of structural materials".

This paper was created as part of the project No. CZ.02.01.01/00/22_008/000463. Materials and technologies for sustainable development within the Jan Amos Komensky Operational Program financed by the European Union and from the state budget of the Czech Republic.

REFERENCES

[1] SCOULLOS, J.M., VONKEMAN, H.G., THORNTON, I., MAKUCH, Z. *Mercury-Cadmium–Lead. Handbook for Sustainable Heavy Metals Policy and Regulation.* Springer, 2001. ISBN 978-94-010-3896-6.

[2] WORREL, E., REUTER. M.A. *Handbook of Recycling: state-of-the-art for practitioners. analysts. and scientists*. Amsterdam: Elsevier, 2014. ISBN 9780123964595.

[3] RAMACHANDRA RAO, S.R. *Resource Recovery and Recycling from Metallurgical Wastes*. Elsevier, London, 2006. ISBN 978-0-08-045131-2.

[4] TRPČEVSKÁ, J., LAUBERTOVÁ, M. *Metal waste and its processing*. Technical University of Košice, Košice, 2015. ISBN: 978-80-553-2365-7.

[5] LAUBERTOVÁ, M. et al. The technology of lead production from waste. *World of Metallurgy*. 2017, vol. 70, no. 1, pp. 47-54. ISSN 1613-2394.

[6] MALCHARCZIKOVÁ, J. et al. Alternative use of lead matte for waste lithium battery processing. In: *METAL 2020: 29th International Conference on Metallurgy and Materials: Conference Proceedings*: May 20-22, 2020, Brno, Czech Republic. Ostrava: Tanger, 2020, pp. 1168-1173. ISBN 978-80-87294-97-0.

[7] KUNICKÝ, Z., KROČA, L. Lead acid batteries recycling in Kovohute Pribram. In *Quo Vadis Recycling: 6th International Conference*, Technical University of Košice, 2017, pp. 182-187. ISBN 978-80-553-3170-6.

[8] *Reference Document for the Ferrous Metals Industry Processing*, 2022. [Online]. [viewed: 2024-01-03]. Available from: https://eippcb.jrc.ec.europa.eu/sites/default/files/2022-12/FMP%20BREF_Final%20Version.pdf.

[9] *Reference Document for the Ferrous Metals Industry Processing*, 2000. [Online]. [viewed: 2024-01-03]. Availablefrom: https://www.mpo.gov.cz/assets/cz/prumysl/prumysl-a-zivotni-prostredi/ippc-integrovana-prevence-a-omezovani-znecisteni/referencni-dokumenty-bref/2017/1/fmp_21-01-09_complete.pdf.

[10] *Releases/transfers of substances*. © Ministry of the Environment, Czech Republic, 2021. [Online]. [viewed: 2024-03-15]. Availablefrom: https://www.irz.cz/vyhledavani-v-irz.

[11] *Circular economy action plan The EU's new circular action plan paves the way for a cleaner and more competitive Europe*. [Online]. [viewed: 2024-05-15]. Available from: https://environment.ec.europa.eu/strategy/circular-economy-action-plan_en.

[12] *Lead's infinite role in Europe's metal recycling industry*. Lead Matters. [Online]. [viewed: 2024-05-15]. Available from: https://leadmatters.org/wp-content/uploads/2020/10/Lead-Matters-Casestudy-Recycling.pdf.