

Regeneration of Lead from Sewage Slimes of Accumulator Factories

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Abstract

Chemical and particle-size composition of slimes from accumulator factory has been investigated. It has been demonstrated that basic part of lead therein is presented by carbonate and oxidic compounds, and in view of fine dispersity of the products, conventional methods of producing lead from slimes are unsuitable. Laboratory tests of two variations of a cementation procedure to reclaim lead from sewage slimes of accumulator factory have been performed. They included the one with intermediate obtaining pure lead sulphate and with direct cementation of lead from a sulphate product. It has been demonstrated that both of variations provide practically complete regeneration of lead to yield marketable products. Advantages and limitations of both variations have been discussed.

INTRODUCTION

Basic operational process for manufacturing lead accumulators also includes, in addition to moulding and treatment of grids and plates, manufacturing of dough, spreading, drying, and cementation of plates, their formation, and assembly of accumulators. All these processes are conducted in aqueous slurries and are accompanied by passing of part of lead compounds in the form of finest suspension into aqueous phase, in consequence of which industrial media need to be subjected to purification from the suspension. Meanwhile, part of lead forms slimes that are caught in special clearing devices of accumulator factories. They differ in their physicochemical properties and processing behaviour from the basic raw material that is processed at lead factories. Moreover, their presence leads to deterioration of production performances, since the high oxidation level, the fine dispersity, and their higher than usual water content promote the formation of rather hard pieces that stick together and clog transport trunks. However, in view of a relatively small volume of the formed slimes, many researchers who dealt with prob-

lems of lead metallurgy ignored the issues of slime processing and lead regeneration from slime. This results in that these slimes occupy a significant volume of apparatuses and dump facilities in a series of accumulator factories. By virtue of the fact that this kind of products, because of their high toxicity and fine dispersity, is to be stored to a burial place with special measures taken, and lead production from them by classical ways is unprofitable and inexpedient in view of the small rates of the output, the issues on their conservation acquire urgent importance.

The purpose of this work is to study the possibility to regenerate lead from sewage slimes of an accumulator factory and the possibility to obtain products that are suitable to be applied at such kind of manufacturers.

ISSUE STATE

During manufacturing lead accumulators, moulding of plates occurs by spreading dough from lead oxides and sulphuric acid over lead plates. The ways of moulding the plates may differ essentially from each other, but their

essence is the same in all the cases: obtaining the lead plates that are filled with dough from lead sulphate. During the course of the operation, a great amount of finely dispersed slimes is generated that incorporate the finest suspension of lead sulphate and that pass to sewage. As of now, according to technological instructions, the sewage is subject to neutralization from residual sulphuric acid by soda solutions to reach the pH 6–7. The slimes that have been filtered off in automatic FPAK-M filter presses constitute light yellow dough with greenish shade with water content of 25–30 %. When dried, the slimes are a fine-grained, readily dusting powder with the density 4500–4700 kg/m³, and the bulk density of 1600–1800 kg/m³.

Chemical composition of the slimes is presented in Table 1; the granulometric composition, in Table 2. When the problem was stated, it was assumed that the produced slimes constitute a sulphate product. However, the data of chemical rational and X-ray diffraction analysis we obtained, as well as those of IR absorption spectra, have demonstrated that the slimes are a mixture of lead oxide and carbonate in their phase composition with an insignificant content of sulphate, as is witnessed also by the small content of sulphate sulphur.

TABLE 1
Chemical composition of slimes

Element	Content, mass %		
	Minimum	Maximum	Average
Lead	63.54	59.72	62.40
Iron	13.1	12.5	12.86
Silicon dioxide	2.54	1.44	1.94
Sulphate sulphur	0.68	0.47	0.59
Copper	0.42	0.39	0.34
Zinc	0.04	0.02	0.03
Antimony	0.025	0.025	0.025
Arsenic	0.004	0.004	0.004
Sodium	0.22	0.16	0.18
Calcium	2.95	2.41	2.83
Potassium	0.15	0.13	0.13
Aluminium	0.30	0.35	0.35
Barium	0.62	0.55	0.57
Gold*	0.08	0.06	0.07
Silver*	0.91	0.41	0.60

*The content is specified in grams per ton.

From compounds of other elements, the slimes include iron hydroxides, calcium carbonate, and silicon acid in appreciable quantities, the compounds passing into slimes at the expense of storm drains that enter in the drain collectors.

The reaction of the aqueous extract was controlled by the extent of soda neutralization of the acid and it was pH 7–8.

As suggested by the given evidence, slimes of sewage represent a completely oxidized, practically pure lead-bearing raw material, which makes them sharply different from usual mineral raw material. In this relation, application of traditional technologies to reclaim lead from these slimes was recognized to be unsuitable from the very beginning. In addition, these factories are located, as a rule, in densely populated areas (for example, St. Petersburg, Tyumen, *etc.*), and setting up the manufacturers that produce lead there, will additionally complicate the environmental situation.

Results of studying the process of lead cementation from sulphate [1] testify that blue lead can be obtained both based on zinc dust, and on iron powder. Previous investigations were conducted considering the application of zinc dust only for cementation, which was ensured by practically closed technological scheme, in which lead production is accompanied with obtaining zinc, *i.e.* with no use of additional reagents. However, application of zinc dust is obviously unacceptable for an accumulator factory, because great volumes of this rather scarce

TABLE 2
Particle size analysis of slimes

Coarseness, mm	Content, mass %
+ 1.00	1.37
–1.00 + 0.63	0.38
–0.63 + 0.40	0.63
–0.40 + 0.31	80.93
–0.31 + 0.20	0.63
–0.20 + 0.16	0.33
–0.16 + 0.10	1.37
–0.10 + 0.074	0.02
–0.074 + 0.041	0.17
–0.041	14.17

reagent are to be used in this case and problems of salvaging zinc vitriol solutions are to be solved. Meanwhile, large metalworking manufacturers that could supply iron chip for cementation are located, as a rule, in the area where accumulator factories exist, and these manufacturers could use the obtained solution of green vitriol as a coagulant in purification of waste and household waters. Therefore, we used exactly this cementing agent in further research.

EXPERIMENTAL

The investigations into cementing extraction of lead from pure compounds have demonstrated that it must be available in sulphate form in order to yield the performance that is reasonable for practical use. In this relation, we developed the variation of generating pure sulphate from slimes. The variation was suggested previously to process mineral lead-bearing raw [2]. This procedure is applied to perform nitrate leaching of lead and its subsequent precipitation by sulphuric acid. Taking into consideration the fact that practically all lead in slimes is present in carbonate or oxidized forms, this flow diagram is free from operations that involve disintegration of sulphide compounds or metallized compounds, and those of sulphate nature as well. Thus, the schema to obtain pure lead sulphate includes the following stages: nitric-acid leaching of lead from slimes at a temperature of 20–25 °C and with the ratio of liquid : solid = (3–4) : 1 and acidifying of the pulp in the end of the operation by fresh nitric acid to yield the reaction medium (pH 2–3) that is stable during the course of 0.5 h. After filtration of the pulp, the cake is dispatched to metallurgical manufacturers for a recovery of valuable components, and the solution, for precipitation of pure lead sulphate by sulphuric acid.

Precipitation of lead sulphate by sulphuric acid was conducted by delivering of strong acid in the solution to the extent of 95 % from the stoichiometric quantity that has been calculated from the lead content of the nitrate solution. The obtained mixture was held over the course of 0.5 h to establish equilibrium and then was filtered off. The solution was fed back to process

new portions of slimes, and the precipitate of lead sulphate was sent to cementation. Table 3 presents the lead distribution data when obtaining pure sulphate. It is evident that extraction of lead in the solution (and, accordingly, to form pure lead sulphate) ranges up to 90.5 %.

When developing a specific flow diagram with the use of one or another technological process, in addition to studying the basic reaction, it is necessary to make also allowance for operations of preparation of feedstock and transformation of the obtained production for the purpose of selling. It is apparent in this case that to conduct the reaction of cementation with satisfactory indexes it is necessary to conduct averaging of the reaction mixture, for this will make it possible to achieve the best contact between the reacting components. In hydrometallurgy practice, this is made by agitating of a reaction mixture during the reaction. However, as shown previously [1], such method in this case leads to a decrease in the speed of the process; therefore, for the purpose of averaging, it is essential to use preliminary mixing of the components of the fusion mixture. It should be noted that when damp, lead sulphate, along with many other fine-grained materials, is prone to pelletization, and stirring the damp product does not permit to attain the required averaging of the fusion mixture. In this relation, to yield the reasonable technology parameters, the sulphate-containing material should be dried to residual dampness of no more than 5 %.

Another important intermediate operation that is common for all flow diagrams to obtain spongy lead constitutes its change to a compact form through remelting. The lead sponge that is received during cementation represents a mixture of fern-shaped and needle-shaped lead crystals with a very developed surface. In air storage, it is quickly oxidized, thus changing to a finest mixture of lead oxides and carbonates, which is accompanied by a strong warm-up of the product. Oxidation rate depends on many factors: the sponge dispersity, residual dampness, storage temperature, *etc.* It is evident that upon the remelting, the oxidized part of sponge will pass into scoria, decreasing thereby the lead yield to marketable metal. To prevent this circumstance, the sponge

TABLE 3

Balance of lead over the products during obtaining pure lead sulphate from slimes

Recycling number	Operation	Introduced quantity, g				Produced quantity*, g	
		Slimes *	Recycled solution*	Nitric acid**	Sulphuric acid	Solution	Residue
1	Leaching	100/62.1	–	40	–	420/56.25	12.5/5.24
	Precipitation	–	400/53.57	–	24.1	450/3.63	–
2	Leaching	100/62.1	400/3.23	12.8	–	420/58.26	15.3/6.02
	Precipitation	–	400/55.5	–	24.3	450/4.09	–
3	Leaching	100/62.1	400/3.63	12.8	–	420/60.54	15.0/6.21
	Precipitation	–	400/57.66	–	26.9	450/5.65	–
4	Leaching	100/62.1	400/5.03	12.8	–	420/60.50	14.5/6.1
	Precipitation	–	400/55.03	–	25.2	450/3.51	–
5	Leaching	100/62.1	400/3.1	12.8	–	420/53.61	15.5/5.9
	Precipitation	–	400/55.8	–	23.4	450/5.94	–

*The first value is the total quantity; the second is the lead quantity.

**Recalculation to anhydrous product.

***Parentheses contain the percentage value.

is recommended to be briquetted right after it has been obtained.

Figure 1 displays a flow diagram that involves all the operations described above for lead reclaiming from slimes to form pure lead sulphate as a commercial product. During its approbation in laboratory conditions with a sample of slimes, the composition of which is given in the above, lead recovery degree into metal (ingot) was of about 80 % from the initial amount in slimes.

We also tried out an alternative variation of processing of sewage slimes by way of cementation, that is, the direct cementation of lead from previously sulphatized feedstock. In this case, preliminary sulphatization of slimes by sulphuric acid in the ratio liquid : solid = 2 : 1 and by means of sulphuric acid delivering into the pulp to reach a pH value of 2–3 that is stable for 0.5 h. After the sulphatization, the pulp was filtered off, the solution was sent to treat new portions of starting material, and the cake was dried up to residual water content of 3–5 %, blended with iron powder, and cementation was conducted under the conditions that were the same as in the procedure described previously. We have failed to obtain briquettes from the sponge by virtue of the fact that, besides the mixture of metals and unreacted lead sulphate, the sponge contained

particles of undissolved residue. Therefore, for the further processing, elutriation of the undissolved residue was performed by means of sponge pulp treatment at liquid : solid = 2 : 1 and with pulp ageing over the course of 1–2 min. Owing to a smaller dispersity, the undissolved residue formed a fairly steady suspension, and the sponge settled quickly onto the bottom. The generated suspension was filtered off, the cake after the filtration was sent to levigation again until the formation of suspension stopped. Thus, the resulting were the undissolved residue and pure sponge that is now easily briquetted and is dispatched to remelting. Figure 2 shows the process flow diagram to recover lead directly from sulphatized slimes.

Upon processing 1 kg slimes under this schematic diagram, the recovery degree of lead to “ingot” was equal to ~75 %.

Both variations of cementation procedure of lead regeneration from slimes show their merits and limitations. To take an example, the scheme with intermediate recovery of pure lead sulphate makes it possible to receive a higher yield and cleanliness of final lead as compared to the alternative variation. However, an additional reagent (nitric acid) and a lot of equipment are needed to realize the scheme. In addition, it is necessary to solve questions of salvaging the solutions with a higher than usual

Lead sulphate	Lead discrepancy***, g	Recovery degree, %
-	-0.61(-0.98)	91.6
74.1/50.5	+0.52(+0.9)	-
-	-1.05(-1.61)	90.3
76.0/51.8	+0.38(+0.6)	-
-	+1.02(+1.5)	90.0
78.0/53.12	+0.55(+0.9)	-
-	-0.54(-0.80)	90.0
78.2/52.23	-0.54(-0.80)	-
-	-0.64(-0.98)	90.0
72.8/49.43	-0.43(-0.77)	90.0

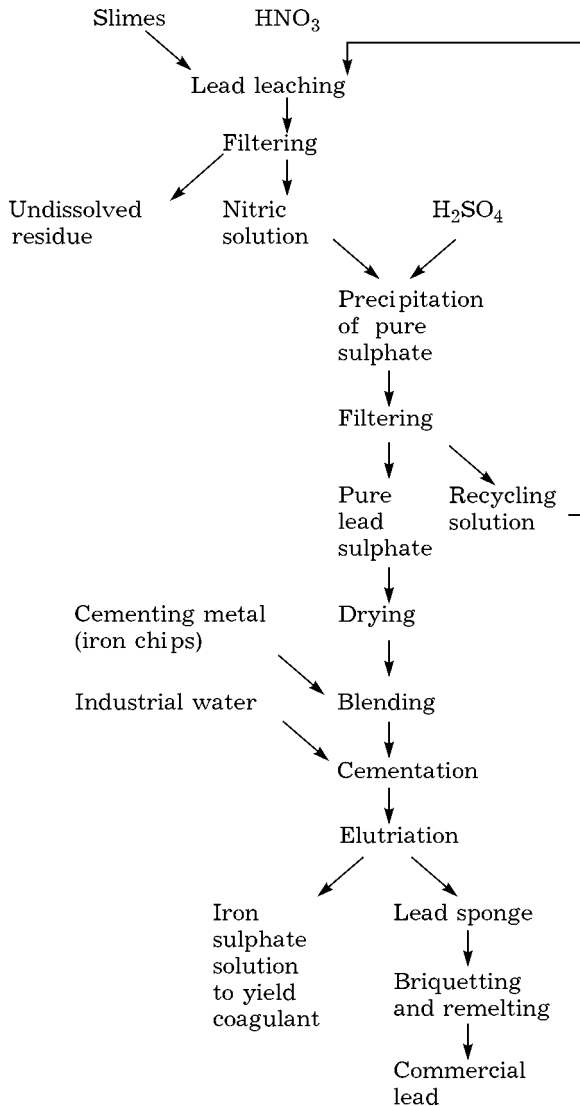


Fig. 1. Flow diagram of lead recovery from slimes with intermediate recovery of pure lead sulphate.

content of nitrates and to prevent nitrogen oxides venting to the atmosphere when they enter in reactors at a stage of leaching of metalized inclusions. Meanwhile, salvaging of solutions after processing of slimes under the scheme with direct cementation of lead from sulphatized raw material can be performed easily within the general technological process at "Accumulator factory" (St. Petersburg). However, additional test should be made in this case on the possible use of the recovered lead as raw material at the factory, since the material will inevitably incorporate higher than usual quantities of impurities (copper and cadmium). By and large, answers to these questions can be given only after larger scale tests during the processing of greater batches of starting materials that can be performed at a pilot setup. Initial specifications for its design have been given to Institute "VNIItsvetmet" (Moscow).

CONCLUSIONS

On a laboratory scale, two versions of cementation procedure to reclaim lead from sewage slimes of an accumulator factory have been tested: the version with intermediate obtaining pure lead sulphate and with direct

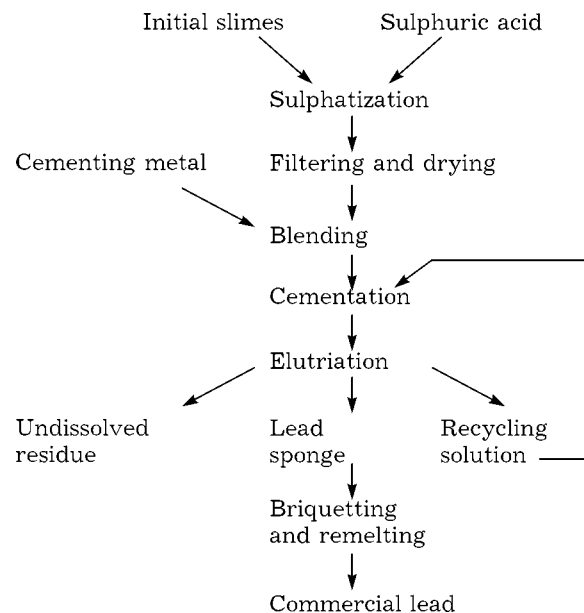


Fig. 2. Flow diagram of lead recovery from slimes with the use of sulphate raw.

cementation of lead from a sulphatized product. It has been demonstrated that both versions provide practically complete regeneration of lead to yield marketable products. Their merits and limitations have been discussed. The final choice for a technological scheme is recommended to be made after larger scale (pilot and trial) tests.

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