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INVESTIGATION OF IMPURITIES PRESENT IN RECYCLING AND REUSING OF SCRAP LEAD FOR ACCUMULATOR INDUSTRY

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Recycling and reusing are the basic strategies of reducing solid waste generated from industries. Millions of batteries containing toxic metals and poisonous wastes are discarded every year in Pakistan. Battery waste deposited in landfills increases the concentration of toxic metals in leachates obtained from landfill base. For this reason, recycling of locally available scrap lead has been focused. During reduction and refining stages, samples were obtained at various stages from a five ton lead smelting pot of an accumulator industry. Various impurities present were determined and removed in order to reuse in accumulators. X-ray fluorescence (XRF) and atomic absorption spectroscopy (AAS) techniques were used to analyze the samples obtained at various stages of recycling. This work has been carried out to reduce these impurities and the refining process has thus been optimized. The lead thus obtained is 99.98 % pure.

Keywords: Lead reduction, Lead refining, Lead-acid battery recycling

1. Introduction

Among all metals, lead is the most recycled one. Even many decades old lead can be recycled for reuse efficiently. Now a days more than half of the lead used comes from recycling. In near future, the recycling of lead will increase tremendously. Most lead for recycling is obtained from lead acid batteries [1]. Spent lead acid batteries contain more than 90% of lead available to get recycled [2]. Other scrap lead sources are pipes, cables, sheets, sludge, slag and dust. Since the last two decades, the recycling of batteries has been changed a lot. For instance, due to certain environmental regulations, the techniques adopted to recycle batteries have been modified to a great extent [3]. The benefits from recycling are numerous. For instance, existence span of lead deposited gets increased; recycling scrap lead is cheaper than obtaining it from its ore; waste generated by recycling spent lead is far less as compared to the waste obtained from primary extraction of lead; capital cost of recycling plant is less than the primary lead extraction plant; energy consumption for recycling is one fourth as compared to the energy used in primary processing of metal; since waste generated during recycling is less, so toxicity towards environment is also less; lead metal can be recycled again and again with no considerable change in its properties. Lead obtained from recycling is more than 90% pure [4]. Some impurities like antimony, arsenic, copper, tin, selenium, silver, bismuth etc. are also present [5].

There are two commonly used methods of lead recycling. The first one is the pyrometallurgical method for lead reduction. All lead samples obtained from batteries alongwith some fluxes, reducing agents, lead waste and slag are added in a furnace for smelting [6]. Impurities present are reduced in the form of oxides. They form dross on surface of molten lead in smelter. Addition of caustic soda removes antimony, tin and arsenic but zinc and selenium remain unaltered. Manganese and zinc are removed by simple oxidation with highly oxygen enriched air. Mechanical stirring during the process is also done for better mixing of additives with impurities. To get rid of copper, Sulphur, in granular form is added alongwith increased rotation of stirrer to generate turbulence in moisture.

The second method is pyrometallurgical method for lead refining. Reduced lead is refined between temperature ranges of 330 °C to 645 °C. Tons of lead are refined in batch-wise operation in a

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Table 1. Analysis results of the first step before and after sample processing .

Element	XRF analysis conc. (ppm) before	XRF analysis conc.(ppm) after	AAS analysis conc. (ppm) before	AAS analysis conc. (ppm) after
Copper	334	329	338	335
Nickel	N.D.	N.D.	N.D.	N.D.
Manganese	339	N.D.	399	29
Antimony	26218	24399	26318	24099
Arsenic	1299	1039	1209	1109
Silver	66	42	64	40
Selenium	71	52	75	56
Tin	363	359	346	340
Zinc	10	N.D	8	N.D.
Ferrous	N.D.	N.D.	N.D.	N.D.

refining pot. At different temperatures, different reagents are added in appropriate amounts [7]. Unwanted metallic impurities get removed after reacting with these reagents. The very first metal removed by reacting with sulphur is copper. To remove tin upto the desired level, air is blown through refining kettle alongwith the addition of some sodium nitrate in it. Air with sufficient oxygen removes antimony and arsenic. Zinc is added to remove silver from lead. Silver can also be removed by oxidation with air. Calcium and manganese are added to remove bismuth. Finally, lead obtained is treated with caustic soda to remove any remaining impurities [8]. Molten lead is then cast into ingots. Release of poisonous chlorine gas during refining increases corrosivity and toxicity [9].This work has been carried out to reduce these impurities and the refining process has thus been optimized. The lead thus obtained is 99.98 % pure.

2. Materials and Methods

A five ton pot made of stainless steel provided with agitator for agitating was used for melting scrap lead. Sufficient supply of oxygen enriched air was ensured. Preferential oxidation of impurities in lead occurred which were then skimmed off as molten slag from top of molten lead in smelter. To determine the impurities removed after oxidation of molten lead, sample was taken out for analysis. Locally available sulphur was utilized from the Qadirabad Gas Fields where it is obtained as a by-product of cleaning of natural gas. X-ray fluorescence (XRF) and atomic absorption spectroscopy (AAS) techniques were used to analyze the samples obtained at various stages of recycling. XRF analysis was done by WDXRF (AXIAS, PANALYTICAL, Netherlands) using IQ Plus software and RSD was better than 6 %. A Varian SpectrAA 300/400 instrument was used for the AAS analysis and RSD in these results was better than 5 %. All chemicals used were obtained from Sigma Aldrich (analytical grade).

3. Results and Discussion

The results of first sample analysis before and after sample processing are given in Table 1. As clear from Table 1, antimony was reduced only by a small amount. Copper, silver, selenium showed no appreciable refinement. The only change worth considering was the removal of manganese and zinc. Further improvement in the process was required to remove antimony which is the major impurity. To increase the extent of refinement, some additives (sodium hydroxide, sodium nitrate, etc.) were added to the molten lead which helped in driving off the impurities in the form of slag. These additives assisted as oxidizing agents so that the impurities may be oxidized and get separated from molten lead more easily and in appreciable amount.

The sample results before and after adding admixtures are shown in Table 2. This analysis depicted that the majority of impurities get removed except copper. Antimony, selenium and tin were appreciably reduced. In order to get rid of copper, sulphur was added. For proper mixing of sulphur with copper, mechanical stirring of molten lead was enhanced. Optimization of agitation rate of agitator alongwith air supply was done. The mechanically

Table 2. Analysis results of the second step before and after addition of additives.

Element	XRF analysis conc. (ppm) before	XRF analysis conc.(ppm) after	AAS analysis conc. (ppm) before	AAS analysis conc. (ppm) after
Copper	329	255	355	259
Nickel	N.D.	N.D.	N.D.	N.D.
Manganese	N.D.	N.D.	20	N.D.
Antimony	24399	3	24199	2
Arsenic	1039	N.D.	1017	N.D.
Silver	42	18	32	18
Selenium	52	3	55	2
Tin	359	5	347	8
Zinc	N.D.	0.67	N.D.	N.D.
Ferrous	N.D.	N.D.	N.D.	N.D.

Table 3. Analysis results of the third step before and after addition of sulphur .

Element	XRF analysis conc. (ppm) before	XRF analysis conc. (ppm) after	AAS analysis conc. (ppm) before	AAS analysis conc. (ppm) after
Copper	225	49	259	42
Nickel	N.D.	N.D.	N.D.	N.D.
Manganese	N.D.	N.D.	N.D.	N.D.
Antimony	3	1	2	N.D.
Arsenic	N.D.	N.D.	N.D.	N.D.
Silver	18	9	18	7
Selenium	3	3	2	2
Tin	5	5	8	3
Zinc	0.67	N.D.	N.D.	N.D.
Ferrous	N.D.	N.D.	N.D.	N.D.

rotating stirrer was fabricated locally and employed so that the molten scrap lead and the flux of additives i.e. sulphur may be churned into the whirlpool by which these may be thoroughly mixed at the vortex. After a few hours, it was seen that impurities became suspended on the top of molten lead.

The sample analysis results before and after addition of sulphur is shown in Table 3. These optimum conditions would lead to the removal of other impurities in addition to copper from molten scrap lead leaving behind purified lead. All drossed impurities were removed from surface of molten lead by mechanical means. For homogeneous distribution, sulphur should be in granular form instead of large pebbles. Sulphur must be added in calculated amount; otherwise it will itself remain in melt as an impurity [8]. Furthermore, to efficiently remove copper, sulphur must be added in the dip of the vortex so that maximum amount of sulphur may get utilized [6,7]. To ensure that scrap lead is free of all major impurities, various samples should be obtained at different intervals from the pot.

4. Conclusion

Minimizing the amount of lead in environment is must for sustainable development and fruitful efforts should be made to recycle the scrap lead in order to reduce the continuous increase in overall inventory of lead through exploration and mining. If recycling and re-melting procedures would not be employed, old batteries and ship breaking, lead scrap etc. would have to be incorporated into landfills; thereby creating a greater hazard than which arises from the small amount of fumes released on re-melting. Scrap lead from local market may be recycled efficiently. The additives should be mixed thoroughly by stirring and by creating turbulence and eddied mechanically. Optimum conditions were used to remove other impurities in addition to copper from scrap lead leaving behind purified lead for reuse. Reduction of these impurities and the refining process has been optimized successfully in this work. The lead thus obtained is 99.98 % pure.

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