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Utilisation of waste battery scrap

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ABSTRACT

The waste battery scrap can be metallurgically treated to separate lead from various impurities such as sulphates, oxides and other metals in scrap. An attempt has been made to smelt the treated battery scrap for recovery of lead as well as for SO_x pollution abatement.

INTRODUCTION

The storage battery scrap is the chief source of secondary lead production. More than 40% of the total lead consumption goes to the manufacture of batteries and around 80 percent of it re-enters the markets as secondary lead. This secondary lead containing antimony is used in the battery manufacture. The battery consists of positive and negative plates which comprises of mainly 86 present PbO_2 and 95 percent Pb respectively, when fully charged. Generally these batteries are scrapped after about two years' use. Apart from metallic lead in plates, connectors, posts etc. lead is present in the form of lead oxide and lead sulphate in the used up batteries. The waste battery scrap treated in the present investigation was mostly free from lead plates and metallic lead and it mainly constitutes the oxides and sulphates of lead. However, the presence of sulphate in the scrap is responsible for excessive fume loss and consequent lower recovery during smelting. The smelting of waste battery scrap is generally carried out in a blast or shaft furnace, a rotary furnace or a reverberatory furnace. In the present investigation an attempt has been made for better recovery of metallic lead from waste battery scrap after its necessary treatment and also to avoid the SO_x pollution during smelting. The smelting was carried out in a pilot scale cupola furnace.

Review of literature

Lead can be recovered from waste battery scrap by electrolysis method as well as smelting route. Ponomarev and Znev[1] obtained compact lead of 99.5% purity from waste powder consisting of lead and zinc by electrolysis. The solution from lead electrolysis was used for zinc extraction. Lead and its alloys can be refined electrolytically[2] using an anode of impure metal or alloy and a cathode on which pure metal is deposited. Recovery of used lead was successfully done by Panckenko and Delimarskir[3] by fused bath electrolysis. Waheed *et al*[4] tested battery wastes by electrolysis in alkaline solution with stainless steel as cathode and mild steel as anode. Dey *et al*[5] leached the battery wastes containing sulphates with 20 percent NaOH solution and electrolysed the leach liquor between stainless steel cathode and graphite anode to recover lead. Lead from the materials of storage battery flat wastes was recovered by Delimackie *et al*[6] by electrolysis in molten NaOH with iron electrodes. Randaccio[7] pantented a process by which different types of scraps, viz. powder, filling etc. of various metals containing lead in sufficient amount can be treated to get higher recoveries by smelting. Reznik and Zaremba[8] suggested processing the battery scrap containing 80% Pb and 2 to 3% Sb in a shaft furnace with natural draft at 900°-1000°C with 2.5% of reduce. The recovery obtained was reported to be 87%. The smelting of battery scrap in an electric furnace without pre-treatment for the elimination of sulphur with high recovery has been claimed in a Japanese patent[9]. The smelting of battery scrap has been practised for a long time, still the recovery of lead is not very good due to the slag-matte losses and sulphur fumes.

Present Investigation

An attempt has been made to recover lead from waste battery scrap after its treatment with wash water and concentrated solution of soda ash. The objective is to mitigate the pollution of sulphur and increase the recovery of lead. Several exploratory trials have been carried out in a pilot scale cupola furnace at the National Metallurgical Laboratory, Jamshedpur, utilizing the waste battery scrap.

Process Details

The first set of experiments was carried out by smelting 60 kg of waste battery scrap without any treatment. The charge consists of battery scrap powder, wood charcoal, soda ash pellets, limestone lumps and mill scale. The typical charge composition was as follows :

Waste battery scrap	-	60 kg
Wood charcoal	-	3 kg
Limestone	-	1.8 kg
Mill scale	-	1.8 kg
Soda ash pellets	-	2.1 kg

The second set of experiment was carried out with treated battery scrap. First, the whole mass of battery scrap was washed with water with a view to remove the sulphuric acid and then with a concentrated solution of soda ash at the ambient temperature in order to remove the sulphur.

In each case, the temperature in the smelting zone was around 1250° - 1300°C and lead was tapped periodically. The typical analyses of waste batter scrap, slag-matte and lead metal is shown in Table-1. Fig.1 illustrates a conceptual flow diagram for the mitigation of lead particulates from exit gases of pilot scale cupola furnace and another conceptual flow diagram for the mitigation of lead particulates as well as SO_x gases is shown in Fig.2.

Table-1 : Typical analysis of waste battery scrap, slag matte and lead metal

	Composition (%)	
	Pb	S
Waste battery scrap	75.04	5.38
Slag matte	25.6 5.95*	-
Lead metal	96.91	2.49

* % Pb in PbO

<u>Possible reactions during smelting</u>

The lead sulphate of battery scrap reacts with soda ash to from lead carbonate which decomposes to form lead oxide. Also lead sulphate reacts with calcium oxide to form lead oxide. Finally the entire lead oxide is reduced by carbon as well as by iron. The scheme of reactions is as follows :

$$PbSO_4 + Na_2CO_3 \longrightarrow PbCO_3 + Na_2SO_4$$
$$PbCO_3 \longrightarrow PbO + CO_2$$
$$CaCO_3 \longrightarrow CaO + CO_2$$

$$PbSO_4 + CaO \longrightarrow CaSO_4 + PbO$$
$$PbO + C \longrightarrow Pb + CO$$
$$PbO + Fe \longrightarrow Pb + FeO$$

RESULTS AND DISCUSSION

As a matter of fact, the smelting of battery scraps has been in practice since long back, but the smelting processes are not economical basically due to low recovery of lead metal - for which both fume and slag matte losses and the sulphate present in the battery are responsible. If the sulphur can be removed from the scrap prior to smelting, the recovery could have increased considerably. In the present situation, the sulphur content in the battery scrap was treated by absorbing it in a highly alkaline solution of soda ash. By doing so it was possible to remove major portion of SO_3 and acid mist along with SO_2, as shown in Table-2. The main reaction occurring are :

$$Na_2CO_3 + SO_2 \longrightarrow Na_2SO_3 + CO_2,$$

$$NaCO_3 + SO_3 \longrightarrow Na_2SO_4 + CO_2$$

Table-2 : Typical analyses of treated and untreated battery scrap and lead recovery

	S (%)	Lead recovery (%)
Without treatment	5.38	72.0
With treatment	2.48	86.5

Table-2 clearly indicates that by treating the battery scrap with alkaline solution of soda ash, sulphur could be drastically brought down and lead recovery improved by 14%. During smelting of treated battery scrap, negligible amount of reddish fumes, which are generally SO_x mist , were coming out through the chimney was observed. However, gas analysis is yet to be done to confirm this observation.

The main source of loss of lead metal is the production of excessive fumes. Recovery can always be improved by collecting the fumes and treating them to recover metallic lead. For this purpose, we have proposed two conceptual flow diagram (Figs.1 and 2) for the mitigation of lead particulate matter, as well as to control the SO_x emission. In the Fig.1, the effluent gases containing lead particulates and SO_x gas come to the dust catcher where lead particulates are arrested. Exit gases from the dust catcher system are brought-down to 150-250°C which finally enters the bag filter assembly where mostly fine lead particulates are arrested. Finally, the exit gas temperature from the bag filter are let off through the stack to the ambient air. A flue gas desulphurization (FGD) system has been proposed to abate the SO_x gases before releasing to the ambient air which is shown in Fig.2. Literature[10] survey shows that lead particulate matter could be arrested in a bed of activated carbon where the exit gas velocity is about 1-1.5 m/s.

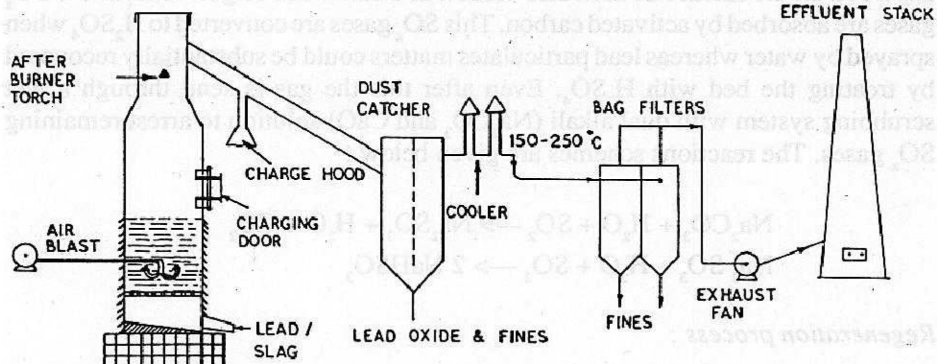

Fig.1 : Conceptual flow diagram for the mitigation of lead particulates

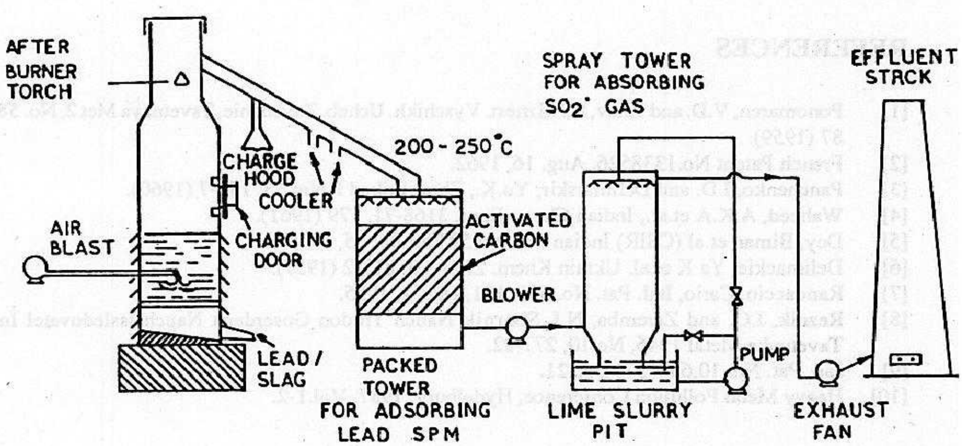

Fig.2 : Conceptual flow diagram for the mitigation of lead particulates and SOx gas

Here the novelty of this technique is that while the lead particulate matters are adsorbed on the surface of activated carbon of bituminous origin whereas the SO_x gases are absorbed by activated carbon. This SO_x gases are converted to H_2SO_4 when sprayed by water whereas lead particulates matters could be substantially recovered by treating the bed with H_2SO_4. Even after this the gas is send through a wet scrubbing system with dual alkali (Na_2CO_3 and CaO) solution to arrest remaining SO_x gases. The reactions schemes are given below :

$$Na_2CO_3 + H_2O + SO_2 \longrightarrow Na_2SO_3 + H_2O + CO_2$$
$$Na_2\,SO_3 + H_2O + SO_2 \longrightarrow 2\,NaHSO_3$$

Regeneration process :

$$2\,NaHSO_3 + CaO + H_2O \longrightarrow Na_2SO_3 + CaSO_3 .\, {}^1/_2\, H2O + {}^3/_2 H_2O$$

CONCLUSION

1. The treated waste battery scrap consisting of mainly the sulphates and oxides of lead was successfully smelted almost without SO_x pollution.

2. The recovery of lead from treated waste battery scrap increased considerably beyond 86.5%

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