

ANALYSIS AND RECYCLING OF LEAD-BASED SLAG FROM BATTERY WASTE FOR TILES PRODUCTION

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ABSTRACT

This paper unveils a measure of risk management through waste minimization from recycling process of a hazardous waste.

Lead-based slag from Exide Battery Nigeria Limited, Ibadan containing heavy metals with the following concentration value on analysis: Pb = 266028ppm, Fe=55871ppm, Sb = 7962 ppm, Cu = 500ppm, Mn=292ppm, and Zn=151ppm was recycled to produce glazed tiles. The slag was finely ground and mixed with clay in varying proportions; kaolin, feldspar, CaCO_3 , ZnO, Na_2SiO_4 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, CaO, Chamotte and bentonite were also added in varying quantities before mixing. The mix was casted under pressure and dried. The brisque temperature was around 800°C for 8 hours. The produced tiles had a white to brown colour before firing and ash-green colour after glazing. The tiles showed high abrasion resistance, good compact strength and are of a quality comparable to encaustic tiles.

Keywords: Lead-based slags, hazardous waste, heavy metals and glazed tiles.

INTRODUCTION

The accumulation of hazardous waste such as Lead-based slag, a by-product in the smelting process of lead in the blast furnace during the major stages of battery manufacture⁴, poses a substantial threat or potential danger to human health or living organisms as defined by Culliname M.J.⁵ in the EPA because they can lethal, non-degradable and their persistence in nature can be biologically magnified or tend to cause detrimental effect⁹.

Hazardous waste which causes an increase in mortality or increase in serious irreversible illness when improperly treated, transported, disposed of or otherwise managed are categorized into (1) Toxicchemicals (2) Radio active (3) Carcinogenic (4) ecotoxic (5) Irritating and oxidizing materials¹.

Lead is not a natural constituent of human body and has no role in normal human physiology, but because it has been mined, smelted and manufactured into useful products for thousands of years, members of industrialized society are

grossly contaminated by this highly toxic metal. Lead and its compounds are cumulative poison.

Environmental lead results to health problem such as stuporous, extreme pale and swollen brain condition known as encephalopathy, the effect of severe lead poisoning as reported by Lois⁸.

Several Federal government programmes aimed at reducing human exposure to lead because it is dangerous to human body at concentration lower than previously believed. Some of its use as alloys and water pipe are in great decline¹⁴. The center for Disease Control has lowered the level of concentration for blood lead to 10ug/dl. A Capacitatively coupled microwave plasma AE spectrometer can be used to determine blood lead with a detection limit of 3 pg in a 5 uL sample¹¹.

The acceptable limit of lead consumption from drinking water is 15ppb (USEPA standard) but some public health experts believe the limit should be even lowered¹⁵.

It is evident that the wastes that are discarded may be significant value in another setting though the ugliness of these waste accumulation site and their potential for damaging our environment and our health have made them the targets of growing public antipathy. But in the long run, an even better reason for doing something about these numerical wastes is the needless loss of valuable natural resources (energy, or raw materials) that they represent which an expanding population and a healthy growing economy requires¹³.

Several factors favour Lead-based slag in this regards their abundance, ready accessibility above the ground, which eliminates the necessity for expensive mining operations and the growing desire of waste producers to find disposal methods which are more socially acceptable than mere dumping.

The concept of waste management is that which is associated with the control of generation, storage collection, transfer and transportation, minimization, prevention, recycling, treatment and disposal of waste in such a manner that is in accordance with the best principle of public health, economic engineering conservation, aesthetic and other environmental contamination that are acceptable by the public⁵.

Stabilization /solidification (S/S) is a term normally used in hazardous waste management to designate technology, employing additives to alter hazardous waste to reduce the mobility of pollutants, thereby making it acceptable for land disposals or other uses.

Catalytic Extraction Processing (CEP) is one of the recycling process obtainable and is an innovative elemental recycling technology that converts organic, organometallics and inorganic wastes, by products, or process stream into marketable (commercial) products like industrial gases, metal alloys and ceramics³.

High strength, light weigh building material are manufactured by Inoue, Norihiro *et al.*⁷ as granulated slag (100 wt, part was mixed with CaO 100, gypsum 5 and silica sand 10 wt parts and a 10-fold amount of water was added. The slurry was heated under agitation, kept boiling for two hours, filtered, molded under pressure of 50 kg /cm² and cured in an autoclave at 180°C for 8 hours to obtain a light weigh building materials having sp.gr 0.83, bending strength 28.9 and 16 kg/cm² compressive strength.

Miyashita reported in his work¹² that crystalline blast furnace slag was mixed with a CaO – Al₂O₃-SiO₂ type binder, then moulded and fired to obtain ceramic product such as tiles, the crystalline slag was ground for 3 hours, mixed with 7 wt percent water glass [1344 – 09-8], compacted at 150kg/cm³ dried and fired at 1100°C after applying fitted glaze (2 mm thick) to obtain tiles with shrinkage at 180°C and 10kg/cm².

Sato, Masao and Kuzulu¹⁶ produced glazed concrete plates from granulated blast furnace slag with blaine finesses 600cm²/g 90, Sodium tripolyphosphate 10, Chamotte aggregate 150 and 40 parts were mixed, shape and cured at 65°C for 5 hours to give a hardened plate having comprehensive strength 675kg/cm². The plate was

Table - 1: Condition used for atomic absorption Spectrophotometric measurement of elements

Element	Wavelength	Slit (mm) width	Lamp current (MA)	Oxidant	Acetylene flow rate (L/mm)	Burner Light (mm)
Silver	328.1	2	3	Air	2.0	7
Cadmium	228.8	3	2	Air	2.1	14
Nickel	232.0	1	8	Air	2.0	7
Bismuth	223.1	2	5	Air	2.1	7
Lead	217.0	3	4	Air	2.4	6
Iron	248.3	1	8	Air	3.3	6
Antimony	217.6	2	8	Air	3.4	7
Zinc	213.9	2	4	Air	13.5	7
Copper	324.7	2	4	Air	1.8	7
Arsenic	193.7	3	10	Air	3.8	14

dried at 250°C for one hour, glazed with Lead-free borosilicate frit and fired at 900°C for 15 minutes to give a product having a surface without pinhole.

Frohlich⁶ in his report used slag from ferrochromium as a raw material for ceramic production phase analysis; chemical composition and particle distribution of the slag were examined.

Reprocessing of the slag diopside (CaO, MgO, 2SiO₂) was examined on a technical scale. After mixing with Kaolinitic and mineral –containing clays at a weigh ratio of 1:1, the product was well milled, spray, dried, hydraulically pressed at 35 Mpa and fired at 1050°C to produced glazed tiles with blending strength > 25 Mpa and moisture absorption 12%.

Venura,¹⁷ presented a paper on how cement-expanding agent are obtained by grinding a mixture of blast furnace slag 100, limestone 130-170 dead burnt gypsum 10-82 and CaF₂ 0.5-4 part and Calcining at 1250.

It is in line with the foregoing, that this research report centers on the production of quality tiles from Lead-based slag (a hazardous waste) to reduce environmental hazard of Lead, to quantify the slag, clay and additives ratio that will form a perfect adhesion with the Lead and the temperature that will be suitable for the tiles glazing.

MATERIAL AND METHODS

Sampling :

Slag samples from rotary furnace were collected from the Exide Battery Nigeria Ltd, Ibadan at their temporary storage site. The slag was heterogeneous in nature, hence random sampling was employed and reasonably large quantity was collected including the hard slag samples. These samples were collected into five polyethylene bags and labeled L, M, N, O & P. A composite sample containing a mixture of L, M, N, O and P was labeled Q. The sample was dried, crushed and ground in an agate mortar. The powdered sample obtained was then sieved through a 2mm scientific sieve. About 10 g of powdered slag particles (Q) was weighed to constant weight after drying at 105°C in an oven for three hours and cooled in a desiccator.

Digestion of Slag Sample:

About 0.5 g of the dried sample was weighed into a 200ml glass beaker. 40ml of Nitric-tartaric acid mixture was added. The mixture was prepared by adding 100ml of conc. HNO₃ to 10g of Tartaric

acid and diluting the mixture to mark with distilled water in a 250ml volumetric flask. The beaker content was heated on a thermostated plate inside a hood until the content was clear. After cooling, the solution was carried out and reagent black was prepared.

Atomic Absorption Spectrophotometric Measurement

Dilution of the digested sample was necessary for the determination of iron & lead. About 2.5 ml was pipetted and diluted into a 100ml standard flask with distilled water prior to absorbency measurement.

Table - 2 : Concentration of Standards used for Analysis of sample

Element	Conc. (ppm) Standard 1	Conc. (ppm) Standard 2
Silver	1.0	2.0
Cadmium	1.0	2.0
Nickel	1.0	2.0
Manganese	1.0	2.0
Lead	5.0	10.0
Iron	2.5	5.0
Antimony	5.0	10.0
Zinc	1.0	2.0
Copper	2.0	-

The concentration of each metal present in the sample was calculated using the formula:

Composition of metal (%) =

$$\left(\frac{CS_1}{AS_1} + \frac{CS_2}{AS_2} \right) X \left(\frac{AS - Ab}{weight} \right) X V_m X D X 10^{-4}$$

where

CS₂ = Concentration of standard 2 in ppm

CS₁ = Concentration of standard 1 in ppm

AS₂ = Absorbency reading for standard 2

AS₁ = Absorbency reading for standard 1

Ab = Absorbency reading for blank

AS = Absorbency reading for sample

V_m = Volume made up to mark

Weight = Weight of sample taken

D = Dilution factor

Manufacture of tiles

Raw Materials Preparation

- Slag:** The slag sample was dried, crushed and screened through a 2mm sieve into fine powdery form.

2. **Clay (cream colour)($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$):** The clay was dried, crushed and ground into fine powdery form. Clay supplies alumina and silica for fusibility, hydrothermal adjustment and plasticity
3. **Feldspar:** Orthoclase – potash feldspar ($\text{K}_2\text{OAl}_2\text{O}_3 \cdot 6\text{SiO}_2$): The hard mineral was processed into fine powdery form. Feldspar provides fusibility, resistance to viscosity and thermal adjustment.
4. **Chamotte:** The old burnt clay was crushed and sieved into fine texture.
5. **Water:** Tap water was used for mixing.
5. Sodium Silicate
6. Calcium Sulphate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)
7. Iron oxide: Dark brown in colour. It is a fluxing agent and aid colourant fusibility.

Procedure for Tiles Making

Mixing and Casting

The raw materials were weighed appropriately and mixed thoroughly in the various proportions in separate containers as listed in Table -3. The mixing was done in the dry form to enhance even distribution of the components particles. Small quantity of water was added and the materials were properly mixed together, well kneaded until a sticky uniform paste was formed. Duplicate samples of tile was produced with small quantity of bentonite added (to aid plasticity) before mixing. The wet clay body was then placed into the cast and pressure was applied on them.

Drying:

The tiles casts were allowed to form. They were then allowed to dry in the sun for 4 - 6 days. This drying process removes water and hardens the tiles normally to permit effective firing in the furnace.

Reagents used as additives and binders in Tile Production

1. Zinc Oxide(ZnO): White in colour and is used for smoothening the material for fluxing (in the medium range of temperature).
2. Kaolin (white clay): Whitish in colour and it supplies alumina and Silica for fusibility.
3. Bentonite: Light brown in colour. It acts as a binder for plasticity.
4. Limestone (CaCO_3): Ash white in colour. It supplies CaO for fluxing while CO_2 is liberated.

Table - 3 : Composition of raw materials for tile production

Tiles Component	C Wt (%)	D Wt (%)	E Wt (%)	F Wt (%)	G Wt (%)	H Wt (%)	I Wt (%)	J Wt (%)	K Wt (%)	L Wt (%)	M Wt (%)	N Wt (%)	O Wt (%)
Slag	100	40	15	-	60	50	30	70	20	10	5	25	35
Kaolin	-	10	5	30	20	10	20	-	-	30	30	20	10
Clay	-	15	25	35	10	10	20	20	20	30	30	30	20
Feldspar	-	30	20	30	5	10	20	-	50	30	35	17.5	18
CaCO_3	-	5	5	5	5	9.5	-	10	10	10	-	5	5
CaO	-	-	25	-	-	-	10	-	-	-	-	-	-
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-	-	5	-	-	-	-	-	-	-	-	2.5	-
Na_2SiO_4	-	-	-	-	-	0.5	-	-	-	-	-	-	2
Chamotte	-	-	-	-	-	10	-	-	-	-	-	-	10
Zinc Oxide	-	-	-	-	-	5	-	-	-	-	-	-	-

Bisque firing:

The tiles were fired after sufficient drying at a temperature between 800°C - 900°C for 8 hours to obtain good fire strength.

Glazing:

A glaze is a glassy layer fused in place on a ceramic ware in order to make the body non-porous, smooth and of good aesthetic disposition. The type of glaze applied on the tiles was earthenware (OPEC) glaze, which was mixed with Iron oxide. The gloss firing was done above 6 hours

at a temperature above 900°C to obtain hard surface coated plates (glazed tiles)

RESULTS AND DISCUSSION

Analysis:

Table - 4 shows the results of slag analysis for heavy metal determination by treatment with Nitric and Tartaric acid mixtures. The metal determined are Zinc, Antimony, Nickel, Manganese, Silver, Cadmium, Copper, Lead and Iron.

Table - 4 : Concentration result in part per million of heavy metal determination in slag sample

Element	Concentration value (ppm) (Mean)
Antimony	7962
Nickel	43
Manganese	292
Silver	6
Copper	500
Zinc	151
Cadmium	5
Lead	266028
Iron	55871

Lead from the result has a value of 266028 ppm and this high value is expected since the slag samples are from lead blast furnace smelter plant. Iron also with a high value of 55871 ppm may be probably as a result of the addition of iron as a secondary reducing agent in the secondary smelter plant. Antimony also have a high value of 7962 ppm which may be due to the addition of antimony to pure lead in order to harden it and also prevent grid fabrication defects and brittleness. Other metals such as Cd, Ag, and Ni were found to be present at low level. These levels are lower than that designated as dangerous by Federal Environmental Extraction procedure toxicity list. The result of this analysis shows that stabilization / solidification method can be used in treating waste slag. Considering the quantity of Iron and lead in the slag, it makes the slag very useful in the manufacturing of bricks, tiles and ceramics, thus presenting heavy metal contamination of the environment.

Evaluation of the produced Tiles

Ceramic tiles are mostly used for protecting walls and floors from abusive wears. It also provides attractive cover for the walls and hitch – free movement. The slag content in the tiles produced determines the colour, strength, smoothness and weight of the tiles. Tiles J with 70% slag by weigh, twisted during firing while tile

C with 100% slag cracked and later broke during drying. The maximum percentage of slag that can be used is 70%. The tiles show varied colours such as white, brown, grey and cream before brisque firing. The different colours are due to the quantity of slag present and the ratio of other materials added. The addition of bentonite improves the plasticity and compactness of the tiles. Tiles with lower slag content are lighter in colour and weight while those with higher slag quantity are heavier and darker. After brisque firing, all the tiles appeared reddish-brown, stronger and lighter than they were before firing.

The glazed tiles with ash-green colour as seen in plate 2 have smooth, shining and impervious surface after gloss firing. Only ten samples with less slag content were glazed properly because those with high slag value vitrify and due to their porosity, easily absorb the glazed applied on their surfaces. Water stability of the tiles was tested by immersing sample containing 40% slag in water for 24 hrs. The tiles remains unchanged as compared to its previous state after drying. The strength and toughness of the tiles were tested using ring test and hand bend test. Only tile F (without bentonite) showed rough edges and unsmooth surface.

Conclusion

Lead smelting slag from battery industry which is confirmed to be very hazardous due to its heavy metal contents, especially lead, could be treated by solidification/stabilization method which helps to limit the solubility of its hazardous constituents and improve its easy handling.

Slag recycling enhances production of quality and affordable tiles and it aids the control of environmental pollution by lead. Hence, government should encourage the maximum recovery of values from this available and unavoidable waste (a disguised wealth) and tile producers should concentrate effort in improving the quality of the product obtained from slag since disposal problem can now be minimized.

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