

# Identification of Risk of Port Logistics in the Republic of Guinea

Jaromir Mares and Aly Hawa Camara

**Abstract**— The following article focuses on the leaching characteristics of the two types of fly ash from the lead metallurgy in the Republic of Guinea which were studied using two standardized leaching tests. These are the European standard EN 12457 and the Toxicity Characteristics Leaching Procedure (TCLP), defined as the U.S. EPA. The leaching tests were complemented by the thermodynamic modeling (EQ3NR), which allowed to determine the solubility of elements in the solution and the degree of the supersaturation of the solution with respect to solid phases. The results of the model were verified by identifying newly created phases using x-ray diffraction and scanning and transmission electron microscope. The PHREEQC-2 model was used for the simulations of arsenic and other elements 'absorption on the newly created amorphous iron oxyhydroxides' surface. The results of the leaching tests show that lead and other metals are extracted in the presence of organic acids and in extremely basic solutions of  $\text{Ca}(\text{OH})_2$ . Based on the results it is not recommended to store the examined waste in the environment of organic - rich soils or to use them in basic conditions

**Keywords**—Crystalline phase, diffraction; diffractogramme; leaching experiments, thermodynamic modeling, X-ray.

## I. INTRODUCTION

NOWADAYS, the environmental protection is a global trend, which is due to the influence of rapid progress in production and technology. The protection is concerned in industrialized countries and this applies to African countries, as well, where the environmental protection is often by the influence of foreign capital-left blend. All countries in the World endeavour to prevent further damage to their natural environment and they continue to introduce legislation protecting the land and the health of the population [1] [2], [3] [4].

### A. Characteristics of present conditions in the Republic of Guinea

A detailed characteristic of the waste is an essential element

The paper was written in the context of the specific research project. The main objective is to present results from research.

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for estimating its influence on the natural environment

Recently, long-term worldwide studies of waste in conditions of dumps of wastes in surface spaces have been subject of many researches in the field of natural environment. Slag, metallurgical slag, and other materials are glazed and intensely analyzed because they contain high levels of heavy metals and other toxic substances.

According to directives of international community, slag and slag slurry are regarded as environmentally dangerous substances. At the same time, they are considered to be commercially useable and are widely used as road construction materials in many countries [5].

The strategy for reprocessing, storage and utilization of wastes in the Republic of Guinea has recently become a topic for serious negotiations with respect to harmonization of legal enactments in the African Union. For many decades numerous places all over the Republic of Guinea have been exposed to a serious environmental contamination. Since 1982, the contamination of underground waters has grown steadily, especially in the vicinity of factories, industrial firms and other important sources of contamination. At several places, new technologies were implemented to reduce the environmental impact of such sources. These protective measures have been and will be partially funded by the Guinean government through the Ministry of Environment, by the companies and by international projects. Such activities play a major role in the funding of environmental studies and evaluation as well. A good example of environmental contamination is a smelting factory in Kankan, which produces huge amounts of wastes because of the metallurgical processing of lead and silver.

Pollution residues and fly ash collected by flue gas cleaning facilities in metallurgical plants are classified as hazardous materials by both the European and the American legislation [6, 7].

Some authors have focused on primary Pb smelter dusts and emissions, and have shown that the chemistry and mineralogy of emissions can be extremely complex, depending on [1] the temperature of the flue gas cleaning process, [2] the nature of the cooling media (water and air) during the dust collection and [3] the chemistry of the blast-furnace charge. The fly ashes residues from primary Pb smelting deriving from Pb–Ag–Zn ore processing are mainly composed of anglesite ( $\text{PbSO}_4$ ) and sulphides (galena  $\text{PbS}$ , sphalerite  $\text{ZnS}$ ) [6]. In contrast, residues from secondary Pb smelting, deriving from scrap

processing, are composed of Pb chlorides (caracolite  $\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}$ , potassium lead chloride  $\text{KCl}\cdot 2\text{PbCl}_2$ , cotunnite  $\text{PbCl}_2$  and laurionite  $\text{Pb}(\text{OH})\text{Cl}$ ). These Pb chlorides are commonly more soluble than Pb sulphides and sulphates [8]. So far, only few studies have been published on the leachability of fly ashes residues from base-metal smelters [9, 10].

Considering the extreme compositional complexity of lead smelting residues, it is difficult to understand their behavior during the mashing even under simple conditions and this behavior may be very important for the environment and technological strategies.

The aim of this paper is to analyse the composition of wastes from critical parts of the Republic of Guinea using suitable analytical methods.

## II. RESEARCH METHODOLOGY

This refers to a research methodology used, subjects of the research, used device and equipment.

### A. *The Object of examination*

The soil samples from the area of the Republic of the Guinea are the subject of the examination in the first place. These samples come from the area of ports. Fly ash samples were collected in Kankan metallurgy plant, currently the best known processing site in the Republic of Guinea. The experiment was designed as a test of solution composition change for identification of preferential dissolution in various phases. This carried out only with tests valid for one year. Types of samples were chosen with respect to differences in the mineralogical composition.

Samples of the weight of 3 kg were collected from each type. Each sample was put in the transparent plastic bag and sent to a laboratory for further analysis. Two different setups were used on the device for this examination: a Czech standard (The European standard EN 12457, in the article labeled as I) and an American standard U.S. EPA (in the article labeled as II). The samples were dissolved into solutions and the extraction was carried out using two types of process.

### B. *Methods of examination*

The phase composition determination using x-ray diffraction uses a fact, that when an x-ray beam passes through a crystalline substance, the diffraction occurs and the form of diffraction depends on the structure of the substance. Every crystalline substance renders a diffraction pattern. The specific diffractogramme characterizes the specific crystalline substance. The phases composition determination can be done by comparing the diffractogramme of an examined substance with a reference set of diffractogramme of known substances. Each component in a mixture produces its own diffraction pattern independently of each other. Thus, the diffractogramme of a mixture is a superposition of

diffractogrammes of particular component as if they were radiated independently for the same time interval. This law applies quantitatively to both, the intensities and the position of diffraction lines, so the method can be used for qualitative phase analysis as well [11].

The quantitative determination of particulate phases supposes knowing their quality Particular phase content determination methodology comes from the method of extensive state values measurement. Magnetographic methods are based on the measuring of a magnetic moment, dilatometric methods are based on a volume measurement, and microscopic methods are based on an analysis of numerical characteristics of statistical sets describing somehow linear dimensions of monophase areas. In comparison with elemental analysis, the x-ray diffraction has a number of advantages. It determines particular crystalline phases directly, so the polymorphic modification of the same substance is distinguished as well. The sample analyzed using x-ray diffraction is not corrupted during the process; therefore it is available for further analysis. The x-ray diffraction analysis requires only a small amount of substance. Beside these advantages over ordinary analytic methods, the x-ray diffraction quantitative analysis has also several drawbacks. It is limited to crystalline substances and achievable precision and detection limit are principally worse compared to the elemental analysis [12, 13].

The extraction solution I with  $\text{pH } 4.93 \pm 0.05$  was prepared by dissolving 5,7 ml acetic acid ( $\text{CH}_3\text{COOH}$ ) in 500 ml deionized water and adding 64,3 ml of 1mol/l sodium hydroxide ( $\text{Na OH}$ ). The Solution was filled with deionized water up to the volume of 1l. The Extraction solution II with  $\text{pH } 2.88 \pm 0.05$  was prepared by dissolving 5.7 ml of acetic acid ( $\text{CH}_3\text{COOH}$ ) dissolved in 1l of deionized water. Deionized water was used for leach preparation, extraction solutions preparation and tools sterilization.

The extraction according to TCLP: The solid-phase: liquid ratio was 20:1. The mixture was being blended for  $18 \pm 2$  hours with turning speed of  $30 \pm 2$  revolutions per minute in temperature of  $23 \pm 2^\circ\text{C}$ . After 6 hours of sedimentation, the final solution was filtered through  $0.45 \mu\text{m}$  thick membrane and stored in a concentrated solution of nitric acid. These two types of leaching test are applied at least twice. Notice, that physical-chemical parameters, such as pH or conductivity, of both solutions were evaluated. The second experiment was done in the laboratory according to the European standard "BATCH" in the HDPE reactors with 200 ml of nitric acid ( $\text{HNO}_3$ ). In each reactor the solid phase was marked and the solid-phase: liquid ratio was 10:1. The Experiment took  $24 \pm 0.5$  hours. Leaches were collected in given time intervals, two replicas were prepared for each interval giving a total of 14 reactors. To avoid a photo-oxidation of acetic acid, these reactors were closed and concealed using special aluminum foil. The reactors were blended using LT2 machine between 5-10 rpm in temperature of  $15\text{-}25^\circ\text{C}$ . The following volumes were recovered from the leach: 20 ml for alkalinity

measurement, 100 ml main cation analysis and 10 ml for main anion analysis. Leach was filtered through a membrane filter with a pore size of 0,45 mm in order to separate particles of organic and inorganic origin. After the filtration, each sample was divided into two part for anions measurement (100 ml) and alkali measurement (50 ml). 2ml of 35% hydro-chloric acid were used to acidity the solution.

Subsequently a measurement was taken in a test machine with constant settings and for as short time as possible in order to maximally reduce undesirable potential of parameter change during the measurement.

### C. Test machines and Equipment

For the analysis of samples we used Bruker D8 diffractometer with a cobalt X-ray tube (Co-K $\alpha$ ,  $\lambda=1.78897\text{\AA}$ ), with large proportional detector. That detector has a 8192 picture elements (pixels) on an area 314 cm<sup>2</sup>. The advantage of electronic detection is that the measured data are instantaneously stored in computer memory without the need of photo-chemical processing of the film with exposed diffractogramme and further photometric analysis. The evaluation was realized using different methods obtaining the data considering extraordinary possibilities of two-dimensional position sensitive GADDS system. Crystallite size influence on quantitative x-ray diffraction phase analysis was also examined.

### III. OVERVIEW OF THE OBTAINED RESULTS AND THEIR EVALUATION

All the samples were analyzed using x-ray diffraction, light optical and electronic microscopy. Using the above mentioned methods the chemical and mineralogical composition of the sample was determined. From Table 1 is seen the chemical composition of the residues. Main chemical components are Pb, Cl, Na and K. In comparison with B residue the sample is enriched by Pb, K and Cd.

From Figures 3 to 6 is possible to see a comparison of selected elements from fly ash A and B. The comparison was according to American and European standards. Only the most relevant volumes of discovered pollutants are shown here. Types of performed examinations are distinguished by color as follows:

Laboratory leaching tests were made for two different types of fly ashes. As we mentioned in the experimental section, a ratio of L:S = 20:1 was used and different ratio of L:S = 10:1 was used on the leaching tests. Solutions from all the L:S tests have shown rapid dissolution of the primary phases. The high ratio leach L:S, which can be used as a model for long-term leachability, showed that primary phases (especially caracolite NaPb<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>Cl and KPb<sub>2</sub>Cl<sub>5</sub>) were dissolved and stable anglesite (PbSO<sub>4</sub>) was created. During leaching the primary amorphous PbSO<sub>3</sub> partially crystallizes and creates a secondary anglesite. This is in compliance with findings, that only anglesite was found historically exposed soils in the

Tab 1: Chemical composition of fly ashes

	n. lab.	14/1	14/2	14/3	14/4
	Sample	A-I	A-II	B-I	B-II
<b>Fe</b>	mg/kg	4830	5190	3985	3520
<b>Mn</b>	mg/kg	174	175	76	77
<b>Mg</b>	mg/kg	96	98	108	108
<b>Ca</b>	mg/kg	1709	1694	194	216
<b>K</b>	mg/kg	38159	38910	23048	22937
<b>Na</b>	mg/kg	22855	28376	212795	214745
<b>Stot.</b>	mg/kg	36191	36218	89500	91329
<b>Cl</b>	mg/kg	204200	202100	201700	204200
<b>Cu</b>	mg/kg	132	149	265	262
<b>Pb</b>	mg/kg	312250	298100	224250	247550
<b>Zn</b>	mg/kg	4110	4280	5085	4900
<b>Cd</b>	mg/kg	6363	6970	4625	4289
<b>Sb</b>	mg/kg	110	98	546	428
<b>Al</b>	mg/kg	248	256	251	209
<b>As</b>	mg/kg	300	248	1416	1348
<b>Si</b>	mg/kg	2086	2163	1462	1656

Legend: A - fly ash 1, B - fly ash 2, I - method according to EU/CR and II - method according to U.S. EPA. In comparison with B residue it is Richter content of Na, As, and Sb. The Enrichment of B residue by Na and S is closely related to the results of the x-ray, which points to the presence of thenardite (Na<sub>2</sub>SO<sub>4</sub>), figure 1. Next, important thing is relative plentitude of caracolite (Na<sub>3</sub>Pb<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>Cl) in the A sample, fig.2

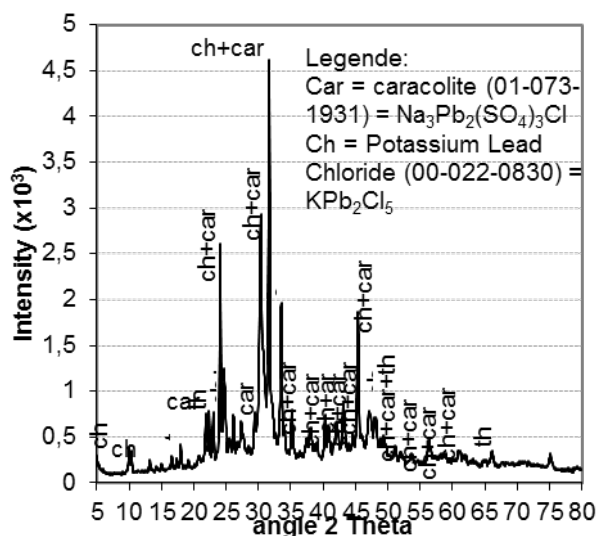


Fig. 1: Diffractogramme of the fly ash sample B

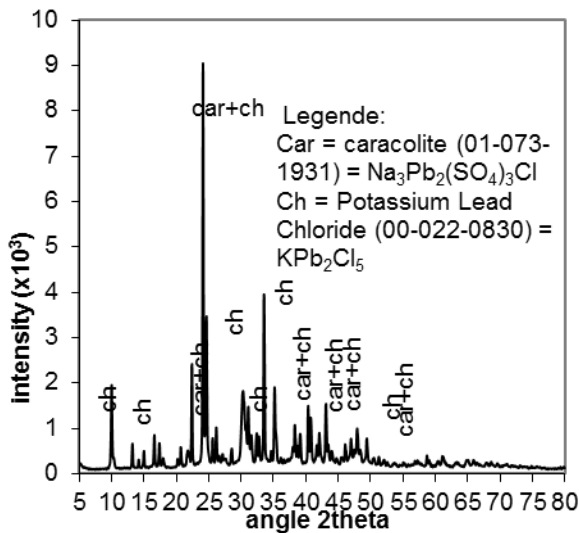


Fig. 2: Diffractogramme of the fly ash sample A

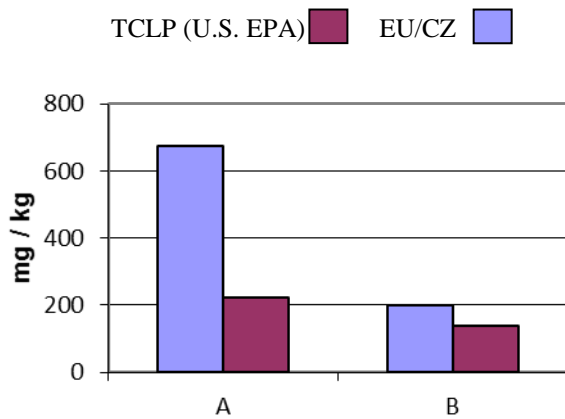


Fig. 3: Cadmium content

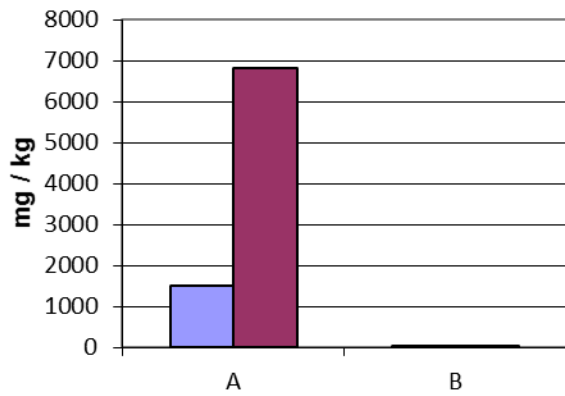


Fig. 4: Lead content

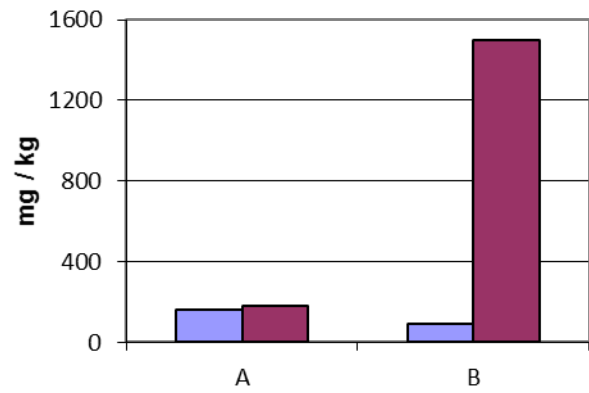


Fig. 5: Antimony content

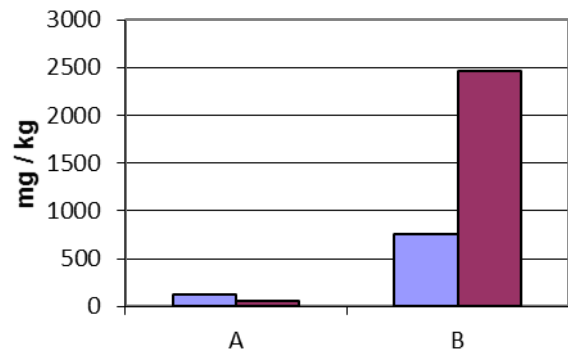


Fig. 6: Arsenic content

vicinity of smelting plants. For fly ash disposal by recycling in reduction blast furnace, the fly ashes can get cleared of soluble salts by washing with  $L/S > 50$  and the remaining insoluble residue (mainly anglesite) could be put back to the production process together with primary lead recycles. Different mineralogical composition, which is dependent on the type of used cooling liquid (pure water, alkaline waste water) influences the reactivity of the fly ash. A fly ash, which was captured after a flue gas had been cooled down by pure water, has higher reactivity than a fly ash that was captured after cooling by alkaline wastewater.

Leaching experiments on fly ash from lead metallurgy „in situ“ in different soil systems have proven, that bags made of a polyamide sieve can be used for fly ash exposition in soil profile research. During one year 62 - 66% of fly ash have dissolved. Especially caracolite ( $Na_3 Pb_2 (SO_4)_3 Cl$ ) and  $KPb_2 Cl_5$  were dissolved creating secondary phases: - anglesite ( $PbSO_4$ ),  $PbSO_3$  and traces of carbonates. Results differences between forest areas and open landscape areas are small. The value of pH is predominant, factor affecting lead leaching and its consequent distribution in the soil profile contrary to cadmium (Cd) and zinc (Zn), leachability of which is nearly independent of the pH. Considerable portion of leached metals (especially Cd and Zn) was found in unstable soil fraction.

## IV. CONCLUSION

Simple standardized leaching tests (EN and TCLP) of the two types of residues occurring in metallurgy, show high levels of dissolution and phase transformations in proceeding processes and give a solution to their interactions. Two methods for determination of low concentration of Sulphur in geomaterials were validated using a set of fifteen certified reference materials. The experiments have shown that ICP OES method is suitable for the determination of gross Sulphur content in geomaterials, including unit level concentrations [ $\text{mg}\cdot\text{kg}^{-1}$ ]. An analytical protocol for matrix impact elimination was also proposed. Foremost this applies to high volumes of Ca and Al in magnitudes of up to tens for percentage by weight. It was proved, that a combustion method with infrared detection is a suitable alternative for volume estimates above 50 mg/kg of sulphur in geomaterials. Leaching of powders using the "batch" was performed on two initial fraction on the two initial fractions with uncontrolled pH using a solution of nitric acid with pH = 2 and deionized water with pH between 5-6. Physical-chemical parameters (pH, Eh and conductivity) and concentrations of elements were monitored over one year. Thermodynamic calculations were made for each solution. The Indices were calculated using suitable thermo-dynamic database according to the EQ3NR. Phases, which were newly created during washing, were studied using physical-chemical techniques for solid matter characterization (XRD, SEM/EDS, TEM). Cerussite coagulation was the main control process, especially with  $\text{pH} > 5$ . Its concentration in the leach can be partially controlled by anglesite formation or adsorption on iron oxy-hydroxides surface. A thermodynamic simulation is performed using PHREEQC-2 computer code and shows that surface adsorption on iron oxy-hydroxides is commonly observed among newly created phases, and it is an efficient control process of arsenic concentration in the leach. Washing test under extreme conditions showed that the presence of organic acids speeds up the dissolution, and this is the cause of the significant mobilization of metals. Both the fly ashes from lead metallurgy were defined as a hazardous waste, especially, the concentration of Pb, Cd, As and Sb significantly exceeded permitted values, which, this can be seen from the charts. However, from the environmental aspect the fly ash originating during from flue gas cooling using alkaline wastewater displays shows higher levels of stability. In contact with water geochemical-mineralogical Pb captures mechanisms occurred. It concerns especially carbonate coagulation (cerussite  $\text{PbCO}_3$  and fergusonite  $\text{PbCl}_2\cdot\text{PbCO}_3$ ) and secondary sulfate coagulation (anglesite  $\text{PbSO}_4$ ), which determine the Pb concentration in the leach. A possible technology of fly ash treatment prior to eventual smelting was proposed. This is based on fly ash and alkaline water interaction, equilibrium with atmospheric  $\text{CO}_2$ , spontaneous precipitation of  $\text{PbCO}_3$  and  $\text{PbSO}_4$  and finally application of the FERROX process [14] for trivalent ironoxyhydroxides precipitation and adsorption of other contaminants from the solution.

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