

Recycling of cathode ray tube in metallurgical processes: Influence on environmental properties of the slag

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Abstract

A potential recycling route for the end-of-life cathode ray tubes (CRT) is its application as a fluxing material in lead and copper smelting processes. Therefore, a thorough study on possible effects of the additional CRT on products and by-products of the metallurgical operation is required. In this paper, influences of CRT addition on mineralogy and leaching behaviour of a fayalite-type slag from a Swedish copper producer are investigated. Mixtures of slag/CRT, in different fractions, were prepared and re-melted in a Tamman furnace. Materials characterization using scanning electron microscopy (SEM) and X-ray diffraction (XRD), and standard leaching tests were done for all samples. Results depict that the main crystalline phase of the slag does not change due to CRT addition. By 10 wt-% CRT addition, leachability of major elements decreases; whereas, that of some minor elements increases. With 35 wt-% CRT addition, leaching of some environmentally detrimental elements make the material unacceptable for construction purposes according to the regulations.

Keywords: Recycling; Cathode Ray Tube; Slag; Leaching; Mineralogy

1. Introduction

The rapid rate of technological developments increases the demand for new electrical and electronic equipment. There has always been a continuous replacement of household appliances with new and improved versions, which causes generation of a high degree of waste electric and electronic equipment (WEEE) [1]. The UNEP (United Nations Environment Programme) estimated the global WEEE generation to be around 50 million tons per year, in 2006 [2]. It is expected that developing countries would triple the amount of their WEEE generation by 2010 (UNEP). A large portion of this waste material is cathode ray tubes (CRT) from televisions and monitors [1,3]. The CRT glass has three basic components with different compositions and varying properties: Panel glass, Funnel glass, and Neck. These parts are joined together by a lead-rich solder glass known as frit [4]. The lead oxide content of the neck and funnel glass reaches 25 wt-% and 20 wt-%, respectively. A high amount of lead is necessary to absorb the UV and X-ray radiation produced by the electron gun. The panel (also called the face) is lead-free, but contains significant amounts of other heavy metals such as strontium and barium [4], making its recycling a challenging task.

There are two different routes for recycling of the end-of-life CRT glasses: closed-loop recycling, when the discarded CRTs are used for production of new CRT glasses and open-loop recycling, when the glass is used for other applications [5]. Earlier work showed that high amount of glass can be used in e.g., brick and tile production, ceramic ware manufacture, or foam glass for insulation [6].

The demand for CRT monitors is still high in developing countries, specifically some populated Asian countries [7], and discarded CRTs from the European Union are exported to these countries for the closed-loop recycling. The re-manufactured CRTs will also reach their end-of-life in future; hence, planning an appropriate recycling route for them now would be beneficial in long term.

Lead and copper smelters use a large amount of silica flux. Due to high content of silica in the CRT glasses, it can be an appropriate substitution for such fluxes [8,9], provided that no adverse effects occur on products (extracted metals) and by-products (where slag is the largest). In the current paper, changes in two of the important characteristics (mineralogy and leaching behavior) of a fayalite-type slag due to application of the CRTs are focused upon. The question is: why are these slag properties important? To save natural resources, use of industrial by-products such as metallurgical slags

Table 1. Content of major elements in the slag, glass, and the mixtures that are used for the experiments, in wt-%

Material	Elements							
	Fe	Si	Ca	Al	Ba	Na	Sr	Pb
Slag	34.0	16.8	4.3	2.1	0.2	0.4	<0.1	<0.1
CRT-Glass	0.2	26.2	0.7	1.1	6.8	6.5	3.9	6.5
*90% slag/10% CRT	30.6	17.8	3.9	2.0	0.9	1.0	0.4	0.7
*65% slag/35% CRT	22.2	20.1	3.0	1.7	2.5	2.5	1.4	2.3

*: Calculated

in construction is widely encouraged by policies and regulations [10,12]. It has been demonstrated that copper slag can be given favorable physico-mechanical characteristics that make it suitable for use in e.g., ballast, cement additive [13], abrasive, aggregates, roofing granules, glass, tile, etc. [14]. The slag that is to be used in any of these applications must fulfill various technical and environmental criteria, where the main concern is leaching characteristics [10]. Therefore, deep understanding of the possible changes in slag chemical composition or phase distribution and consequent changes in the leaching properties is essential.

2. Experimental

Slag and glass samples were supplied by a Swedish base and precious metals producer, the Rönnskär smelter of Boliden Mineral AB. Main products of the Rönnskär smelter are copper, zinc clinker, lead, gold, and silver, while sulphuric acid, liquid sulphuric dioxide, and Iron sand (granulated slag) are some of the by-products [15,16]. Slags are generated in e.g., the electrical and flash smelting furnaces. The slag tapped from the flash smelter is slow-cooled and transported to the Boliden concentrator for copper extraction by grinding and flotation. The generated slag in the electrical furnace is charged to the fuming furnace, where it is treated by reducing gases to produce zinc clinker. The fumed slag is tapped from the fuming furnace into the settling furnace for further cleaning. Afterwards, the slag is water-granulated and currently sold as e.g., construction material [16]. Primary and secondary raw materials with complex composition are treated at the smelter; the operation is thus adapted to handle impurities. The investigated slag was taken from the settling furnace after the slag-fuming process and is an iron-silicate or so called fayalite-type slag. The CRT glass is a mixture of panel and funnel glasses. In order to be able to study the effects of CRT on slag, three different samples were prepared. One reference sample, which was merely slag without any additive, and two different mixtures of 90 wt-% slag/10 wt-% CRT

and 65 wt-% slag/35% wt-% CRT. Chemical composition of the used slag, CRT, and the mixtures are presented in Table 1.

The prepared samples were placed in alumina crucibles and re-melted in a Tamman furnace. The heating was done in two stages: a non-steady heating up to 600°C and further heating at a steady rate of 5°C/min up to 1400°C. The samples were then cooled down to 1000°C at 10°C/min, and left in the furnace to reach the room temperature (semi-rapid solidification).

Structural properties and elemental content of the materials were studied using scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS), for semi-quantitative analysis. A Philips XL 30 SEM with accelerating voltage of 20 kV was the applied instrument. X-ray diffraction (XRD) patterns of the samples were recorded by a Siemens D5000 X-ray diffractometer, with copper K_{α} radiation (40 kV, 40 mA) as the X-ray source. 2-theta-scale range was between 10° and 90° in 0.02°/step by counting 2 s/step. The phase identification was made by reference patterns in an evaluating program supplied by the manufacturer of the equipment.

For leaching tests, large pieces of semi-rapidly solidified slag were crushed to a particle size less than 4 mm and leached according to the single-stage prEN 12457-2 leaching test [17] at L/S (liquid to solid ratio) of 10 l/kg. Leachates were filtered and sent to a certified laboratory, ALS laboratory group, Sweden, to analyze. To assure representativeness of the leaching results, all trials were done in duplicate, where there was good agreement between the results.

3. Results

3.1. X-ray Diffraction (XRD)

The XRD patterns of all samples are shown in Figure 1. According to the evaluating program, major phases of the samples are identified as fayalite (Fe_2SiO_4), calcium silicate and spinel solid solutions.

Fayalite is the main phase in all three samples. Identified calcium silicate is a solid solution of different silicates including: augite,

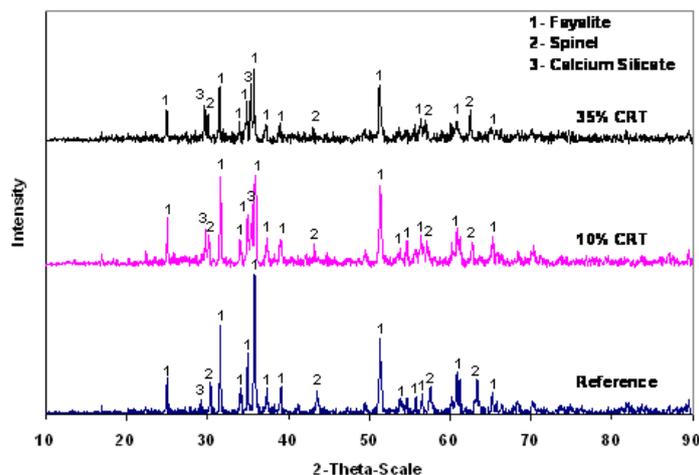


Figure 1. XRD pattern of the slag and slag/CRT mixtures.

Ca(Fe,Mg)Si₂O₆, petedunnite, CaZnSi₂O₆, gehlenite, Ca₂Al₂SiO₇, esseneite, Ca(Fe_{1.4}Al_{0.6})SiO₆, and calcium aluminium silicate, CaAl₂SiO₆, which are named, generally, as calcium-silicate-based solid solution. In the reference sample, this solid solution is rich in gehlenite and calcium aluminium silicate, while in the sample with 10% CRT addition it is augite-rich and in the sample with 35% CRT, its main constituent is esseneite.

Low intensity peaks of spinels are also detected. Spinel is series of solid solution with general formula of AB₂O₄, where A and B represent +2 and +3 cations, respectively. Due to its face centred cubic (FCC) unit cell, occupying cations in spinel’s structure are quite susceptible to be substituted by other cations [18,19]. As a result, specifying the exact composition of an individual spinel, in complex materials such as slag, is not recommended, and they are named, generally, as spinel.

Spinel peaks remain almost the same in the XRD patterns of the samples with different amount of CRT addition.

Overall, the intensity of the major peaks of the patterns decreases by addition of more CRT glass, which can be an indication of formation of an amorphous structure in the material.

3.2. Scanning Electron Microscopy (SEM)

EDS mapping was applied to study the elemental content of the samples. EDS mapping of the reference sample is shown in Figure 2. Three main phases could be identified. The brighter lamella-like phase, which is labelled as “1”, shows the coexistence of iron and silicon. Phase “2”, cubic structure, is iron- and aluminium-rich, where silicon and calcium are absent. Phase “3”, darker matrix, is rich in calcium, aluminium, and smaller amounts of silicon.

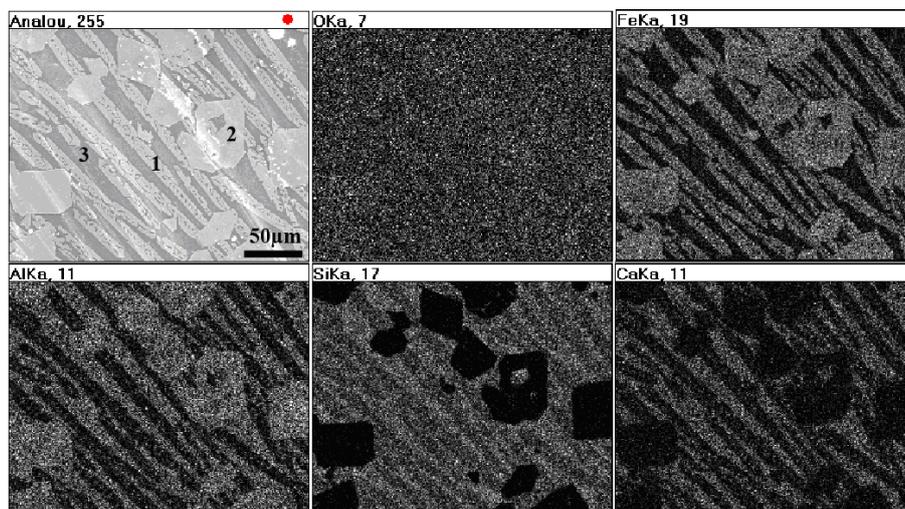


Figure 2. EDS mapping of the reference sample, slag without any additive; Magnification × 520.

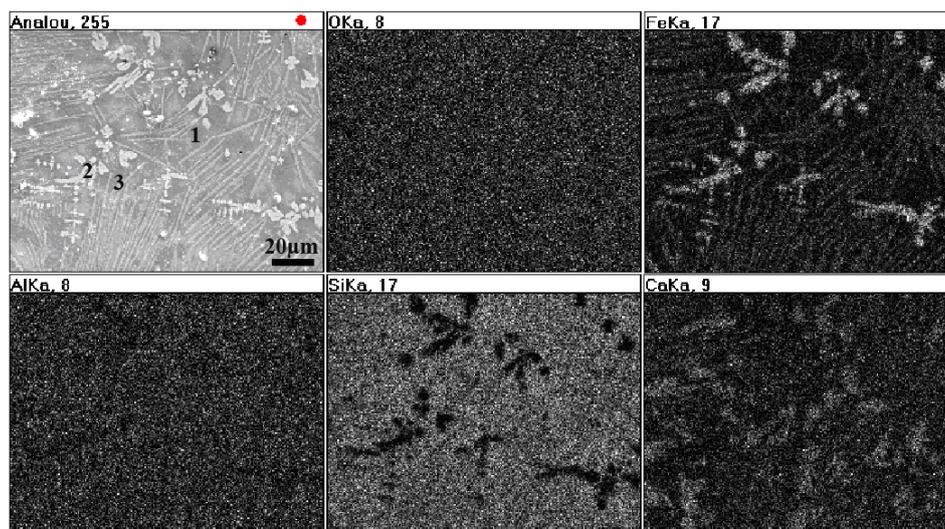


Figure 3. EDS mapping of the mixture of 65 wt-% slag/35 wt-% CRT; Magnification× 800.

The EDS mapping of the sample with 10 wt-% CRT addition is similar to the reference sample (no distinguishable change could be observed). With higher addition of CRT (35 wt-%), a more homogenous structure is formed, Figure 3. In this sample, phase “1” (brighter lamella) is present in smaller dimensions and distributed over the whole area of the sample. Phase “3” shows no considerable change, still appears as the matrix. Phase “2” is present with smaller dimension and its iron content increases for the samples with higher CRT addition at the expense of aluminium (the concentration of Al decreases). Generally, it can be said that the structure goes toward a more homogenous and even distribution of the elements by addition of CRT.

3.3. Leaching

Leached amounts of different elements in µg/l of the leachates are shown in Table 2. Most of the elements show a trend of increasing leachability upon more addition of CRT. Leaching of calcium decreases, continuously, by CRT addition. Leaching of iron and silicon

decrease by 10 wt-% CRT addition and then increase by higher additional CRT.

4. Discussion

A comparison of detected phases in the XRD patterns (Figure 1) and EDS mappings (Figures 2 and 3) enhances the identification of the actual phases that are present. Phase “1”, which contains Fe and Si in the EDS maps, corresponds to the detected fayalite phase in the XRD patterns. Phase “2”, where Si and Ca are absent and the content of Fe is high, corresponds to the spinel phase of the XRD patterns. The calcium-rich phase, “3”, corresponds to the detected calcium silicate phase in the XRD patterns.

Elements such as strontium, barium, and lead were distributed over the whole investigated area of the samples at very low concentration and could not be considered as phase forming elements.

The observation that the mixture of 90 wt-% slag/10 wt-% CRT showed similar morphology as the reference sample means that

Table 2. Leaching results in µg/l.

Element	Reference	10% CRT	35% CRT
Ca	7620	6810	4720
Fe	74	55	137
Na	334	967	2640
Si	3950	1490	1970
Al	721	1510	1790
Ba	10	114	356
Pb	2	12	53
Sr	12	123	541

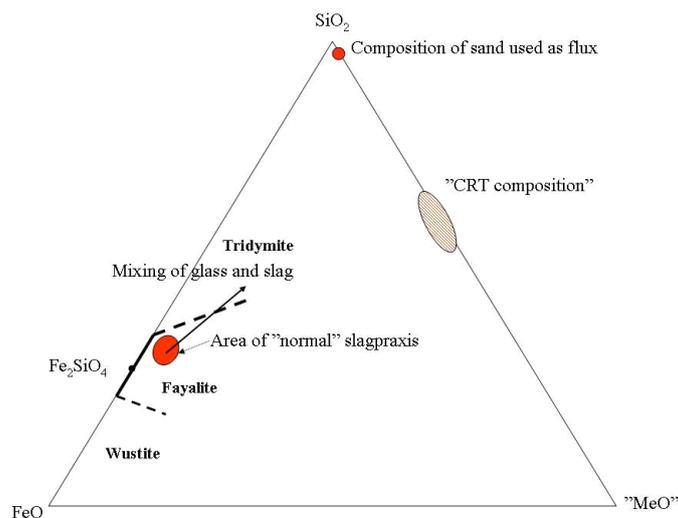


Figure 4. Schematic diagram showing the areas of normal slag praxis and CRT composition. The arrow shows the direction in which the composition of slag would change due to CRT addition.

low contents of the CRT addition would not affect the mineralogy of the samples dramatically. At higher CRT addition (35 wt-%), both EDS mapping and XRD analysis reveal that the samples go toward a glassy structure. Or it can be said that the main phases of the slag (fayalite and spinel) are embedded in a glassy matrix. This point is confirmed by lower intensity of the main phases' peaks in the XRD pattern of the sample with 35 wt-% CRT, and also homogeneous structure and even distribution of the elements in the EDS mapping.

From a thermodynamic perspective, the material changes its initial primary crystallization field with 35 wt-% CRT addition. Figure 4 shows a schematic pseudoternary phase diagram of the "FeO"-Al₂O₃-SiO₂ system, which is constructed based on the diagram reported by Levin et al. [20], in equilibrium with metallic iron. In the reference sample and the one with 10 wt-% CRT addition, the material lies in the primary crystallization field of fayalite. With higher proportion of CRT glass, the composition will change to the primary phase field of tridymite, yielding a different structure.

Increasing the CRT addition changes the composition of the spinel phase toward magnetite-based solid solution, as concentration of iron in this phase increased and that of aluminium decreased. It can be stated that aluminium iron oxide, Fe(Fe, Al)₂O₄, and hercynite, FeAl₂O₄, fractions of spinel solid solutions are converted to magnetite, FeFe₂O₄. At the same time, the major constituent of the calcium silicate solid solution is also changed from augite, CaFeSi₂O₆, in the sample with 10 wt-% CRT, to esseneite, CaAl₂SiO₆, in the sample with 35 wt-% CRT. This means that there

is an exchange of aluminium between spinel (which initially contains high amount of aluminium) and calcium silicate solid solutions (refer to EDS maps).

Leachability of major elements (iron, calcium and silicon) decreases by addition of 10 wt-% CRT. Calcium and silicon are the main matrix former elements of the investigated samples; considering the indication that material is changing toward a more amorphous structure and the fact that silicon is the main network former element of most of the glassy structures, explains the lower leachability of these two elements due to 10 wt-% CRT addition.

Spinel is considered to be durable and less soluble than other phases [21-23], which explains the lower leachability of iron and higher leachability of aluminium in the sample with 10 wt-% CRT addition (as iron substitutes aluminium in spinels).

Most of the minor elements such as lead, strontium and barium leach in higher quantities with 10 wt-% CRT addition. Concentrations of these elements are higher in the sample with 10 wt-% CRT addition than the reference sample, and their leaching amounts are also increased in this sample; this means that they cannot be bound in stable mineral phases. As leaching of major elements decreases and there is no sharp increase in leachability of the minor elements for the sample with 10 wt-% CRT addition, the material is still tolerable for construction purposes according to the environmental regulations [24].

For the sample with 35 wt-% CRT addition, except calcium, all the other elements leach at much higher quantities than the sample with 10 wt-% CRT addition. The material

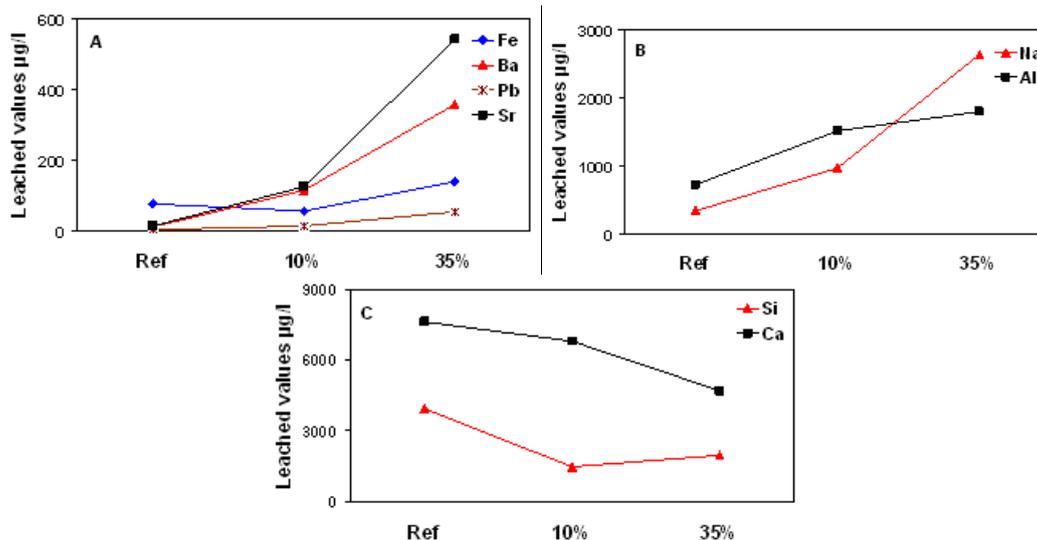


Figure 5. Leached values of different elements in µg/l.

changes the primary crystallization field by 35 wt-% CRT addition; besides, an amorphous or glassy phase is also formed in this sample. These are the main changes that cause a higher leachability for this sample. It has been proven that in the presence of a glassy phase in the sample, leachability of the minor elements is extremely dependent on the aqueous chemistry, chemical reactions, and possible secondary phases that can be formed [25]. Therefore, finding a mineralogical explanation for most of the elements is not straightforward. It seems that when the material changes its primary crystallization phase field from fayalite to tridymite, the reaction tendency with the aqueous solution is increased; thereafter, more elements dissolve in leachate. In other words, the leaching is controlled by mechanisms other than mineralogy, which are beyond the scope of this paper.

Figure 5 shows the leached values of the elements in different samples. There is a sharp increase in leachability of some elements in the sample with 35 wt-% CRT addition. Leached amount of lead is not acceptable according to the environmental regulations if the slag is to be used in construction applications.

5. Conclusions

The results from XRD and SEM analyses are in agreement, confirming that the dominating crystalline phases in the reference slag and the mixtures of slag and glass are fayalite, calcium silicate and spinel solid solutions. The main constituents of these solid solutions are changed by CRT addition. In other words, aluminium was dissolved from the spinel solid solution, aluminium iron oxide, Fe(Fe,

Al_2O_4 , into the calcium silicate matrix to form esseneite, $\text{CaAl}_2\text{SiO}_6$.

In the sample with higher CRT addition (35 wt-%) the contents of fayalite and spinel are lower and an amorphous phase is formed. The results indicate that with addition of up to 10 wt-% CRT, the composition of the melt remains in the primary crystallization phase field of fayalite, while it changes to tridymite phase field with 35 wt-% CRT.

From a leaching point of view, while the material is still in the fayalite primary crystallization field, the leaching of the elements, including the environmentally detrimental elements, are in a tolerable range. By higher addition of the CRT (35 wt-%), more reaction tendency with the aqueous solution increases the leachability of these elements.

According to the results of the current experiments, CRT addition up to 10 wt-percent would not change the mineralogy or adversely affect the leaching characteristics of the slag. 35 wt-percent CRT addition forms a more complex material with a glassy inclination that increases the leachability of almost all elements and is not appropriate for construction applications.

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