Recovery of Gallium from Smartphones – Part I: Thermal and Mechanical Pretreatment

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Abstract

The aim of this study was the investigation of possibilities to produce a gallium-rich intermediate product from discarded smartphones. For this purpose, pyrolysis followed by mechanical treatment including ball milling and sieving were performed. It was found that the applied procedure is suitable to enrich Ga, Au, Nd and Dy in a fine fraction, whereas the majority of Cu, Fe, Ni and Sn is collected in the coarse fraction. During a subsequent metallurgical assessment, a metallurgical processing route was developed with respect to selective winning of Ga as well as the recovery of rare earth elements, Cu and precious metals.

1 Introduction

Regarding the metal recovery from large amounts of waste electric and electronic equipment (WEEE) pyrometallurgical smelting and refining along the copper route typifies the state of the art process in europe. The bath smelt technology enables an almost complete recovery of copper and precious metals (Au, Ag, Pt, Pd) which are concentrated in the copper phase. Less noble metals such as Sn, Pb and Zn are enriched in slag and flue dust respectively and can be extracted from those streams as well [1]. Furthermore, it is well known that WEEE also contains a wide spectrum of several technology metals, namely indium, gallium, tantalum and rare earth elements which occur in trace amounts only. These elements are dissipated during the pyrometallurgical smelting process due to their low concentration and their ignoble character [2, 3].

In contrast to precious elements, however, the mentioned trace metals possess a relatively low market price so that recyclers are not encouraged to take elaborate measures regarding a recovery from the copper process. Paradoxically, indium, gallium and some rare earth elements are classified as critical metals which refers to their technological importance, a certain supply risk and a recycling rate of 0 % [4].

Taking gallium into account, it is predicted that there will be a slightly increasing demand for its use in electronic applications. The proceeding establishment of 4G (fourth generation) wireless technology in the field of information and communications technology makes special requirements on the performance of particular devices – especially on smartphones as a wide distributed consumer product. In order to maintain high data transfer rates, power amplifiers based on GaAs (gallium arsenide) are an essential key technology and will also play an important role in the next years as 5G will be introduced to the market [5, 6]. Although the worldwide market for smartphones might be saturated at the moment [7], there will still be a demand for GaAs in future due to the ongoing standardization of 4G / 5G and – much more substantial – the predicted growth of GaAs application in optoelectronics [8]. Apart from that, there are several smaller market fields for Ga like photovoltaic, gallium nitride (light-emittig diodes) and other semiconductors [9].

Currently, primary resources in china are able to cover the demand for pure gallium [10], but concerning the facts of criticality and a certain domestic supply through discarded electronic devices such as smartphones, it appears to be reasonable to think about an independent source for gallium.

The background of this work is the idea of preprocessing WEEE previous to pyrometallurgical smelting in order to separate and concentrate gallium. As input material, smartphones were chosen for several reasons:

- for a proper experimental study, an input material with a reliable and relatively constant amount of Ga is needed;
- different challenging properties of WEEE are combined in one device: high complexity of materials and elements, encapsulation of components and low amount of target elements;
- due to these aspects, the results from this study can be transferred to other, less challenging materials;
- discarded smartphones and similar products (i.e. tablet PCs) will a occur in the future.

Recent research activities already identified pyrolysis as a promising option for a preprocessing step. By means of pyrolysis, the material is heated to temperatures between 300 and 800 °C in an oxygen-free atmosphere. The thermal treatment causes a degeneration of polymers (plastics) or in other words the cracking of long hydrocarbon chains into smaller volatile molecules. The latter can leave the system through the off gas. In their study, Diaz et al. concluded that degeneration of the plastic fraction of printed circuit boards (PCB) enables the breakup of metal-plastic- and glass fibre-plastic-composites so that a ferrous and non-ferrous metal fraction can be obtained by mechanical treatment [11]. Another approach focusses on the recovery of indium from discarded smartphone displays via halogenation and volatilization during pyrolysis. It was found that a complete indium separation from the displays can be obtained without any additional halogenation agent by applying a sufficient high process temperature [12]. Therefore, it is worth to follow the concept of pyrolysis and examine if it is applicable for a separation of gallium. Simultaneously, the fate of other valuable metals (Cu, Sn, precious metals) must be considered as well.

By reason of the encapsulation of the GaAs-bearing integrated circuits (IC) on the smartphone's PCB, it is expected that Ga will remain in the solid pyrolysis residue. Similar to the work of Diaz et al. the procedure in this study comprises pyrolysis of the smartphones followed by a combination of grinding and sieving in order to investigate, if gallium can be concentrated in a particular sieve fraction.
For the planned works, information about the composition and the content of single metals in smartphones are required and therefore presented in the following.

2 Elemental Composition of Smartphones

So far, there have been only few scientific works on the elemental composition of smartphones. Two detailed studies were conducted by Bookhagen et al. [13] and Holgersson et al. [14]. Both focused on PCBs because this compound holds the majority of (valuable) metals in a smartphone. The values depicted in Figure 1 are based on the data generated by Holgersson et al.. For this work, data was evaluated in a different way so that three main groups of materials turned out: Polymers, glass / ceramics and metals. Metallic elements below 1 wt.-% were summed up as trace metals. All values are given in wt.-%. The particular trace metals are listened in Table 1

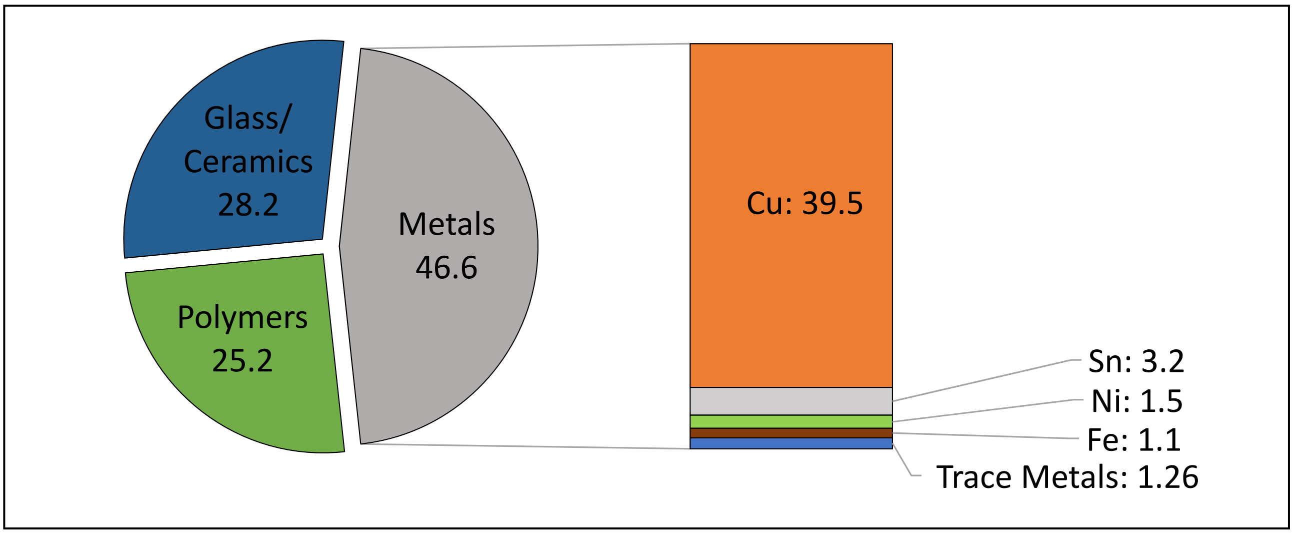

Figure 1: Composition of smartphone PCB; values in wt.-% [14]

Table 1: Concentration of trace metals in smartphone PCB in ppm [14]

	Ag	As	Au	Cr	Pb	Pd	Pt	Rh	Sb
conc. / ppm	2773	141	1083	1219	260	55.4	0.8	8.5	30.4

As can be seen, Holgersson et al. provided no information on gallium, but on arsenic. If it is assumed that all arsenic exists in shape of GaAs and the mass ratio Ga : As is 0.93, according to the molar masses, an empiric Ga concentration of 131 ppm can be calculated. Additionally, Bookhagen et al.

determinated a Ga content between 100 and 300 ppm with an average of 200 ppm. Concerning the portion of the PCB relating to the whole smartphone, Bookhagen et al. specify values of 11, 13 and 18 wt.-%, whereas Holgersson et al. indicate 13.5 wt.-% for a PCB (without metal covers). Therefore, an average weight proportion of 14 % is assumed in this work. Using this value, the gallium content of a smartphone can be estimated around 18.3 ppm.

3 Materials, Process Concept and Experimental Work

The smartphones used for the experiments originated from different manufactures and years. For safety reasons they were purchased from collecting companies without batteries. Figure 2 illustrates two different processing routes which were executed.

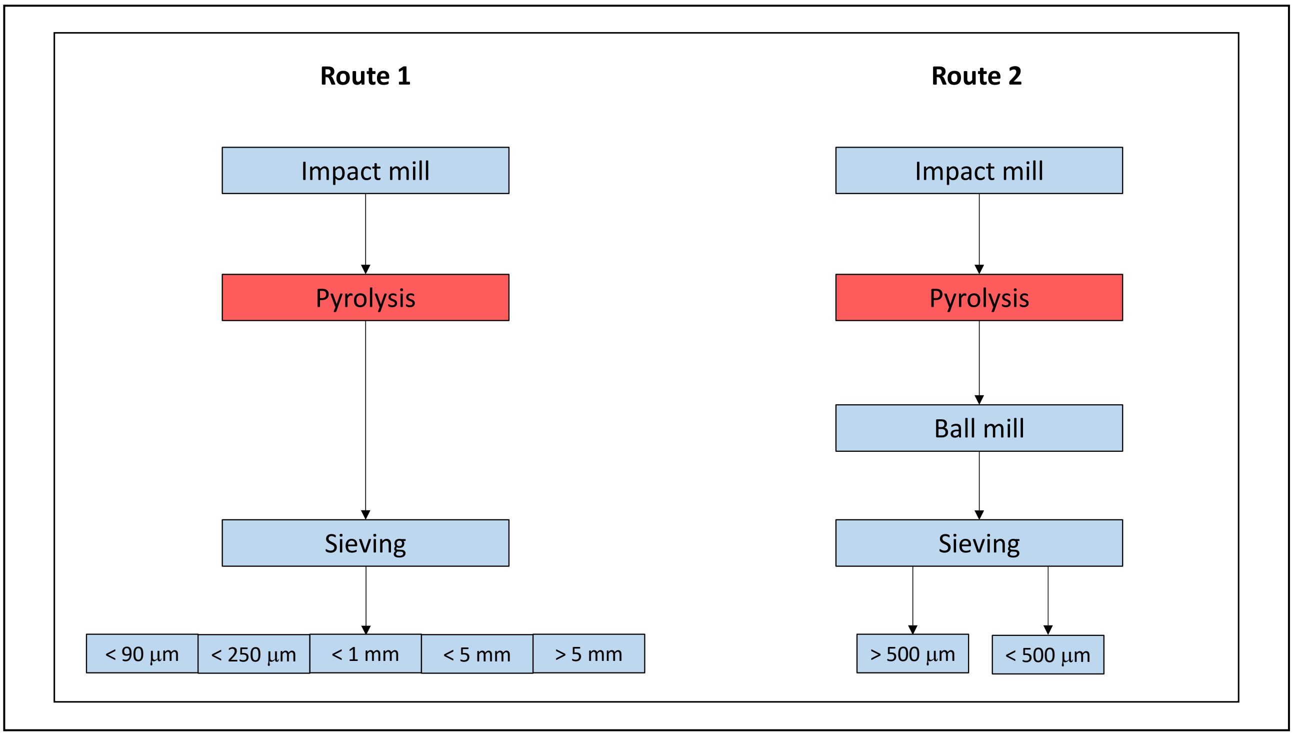

Figure 2: Processing routes for smartphones

Both routes start with a crushing step by means of an impact mill in order to crack the casings and expose single components – especially gallium-containing PCBs (see Figure 3). Afterwards, the crushed devices were pyrolyzed in charges of 4.5 kg. In case of route 1 only one charge was treated, whereas regarding route 2, three charges were pyrolyzed, resulting in a total input mass of 13 kg. The reason for the increase of charges in route 2 are the results of route 1 as will be explained later.

Figure 3: crushed smartphones after impact mill

3.1 Pyrolysis

Corresponding to Figure 4, pyrolysis of the crushed smartphones was performed in a 24 L steel reactor which was inserted into a resistance furnace. According to the low bulk density of the crushed smartphones, a maximum amount of 4.5 kg could be charged into the vessel. The off-gas cleaning system consisted of a water-cooled condenser, a wet scrubber and a torch for post combustion. To avoid a condensation of gaseous organic compounds inside the off-gas duct, it was electrically heated to 350 °C. During the process, the reactor was purged with a constant flow of 10 L nitrogen per minute and heated up to 570 °C by applying a heating rate of 300 °C/min. After reaching 570 °C the temperature was maintained for 90 min, before the furnace cooled down to room temperature.

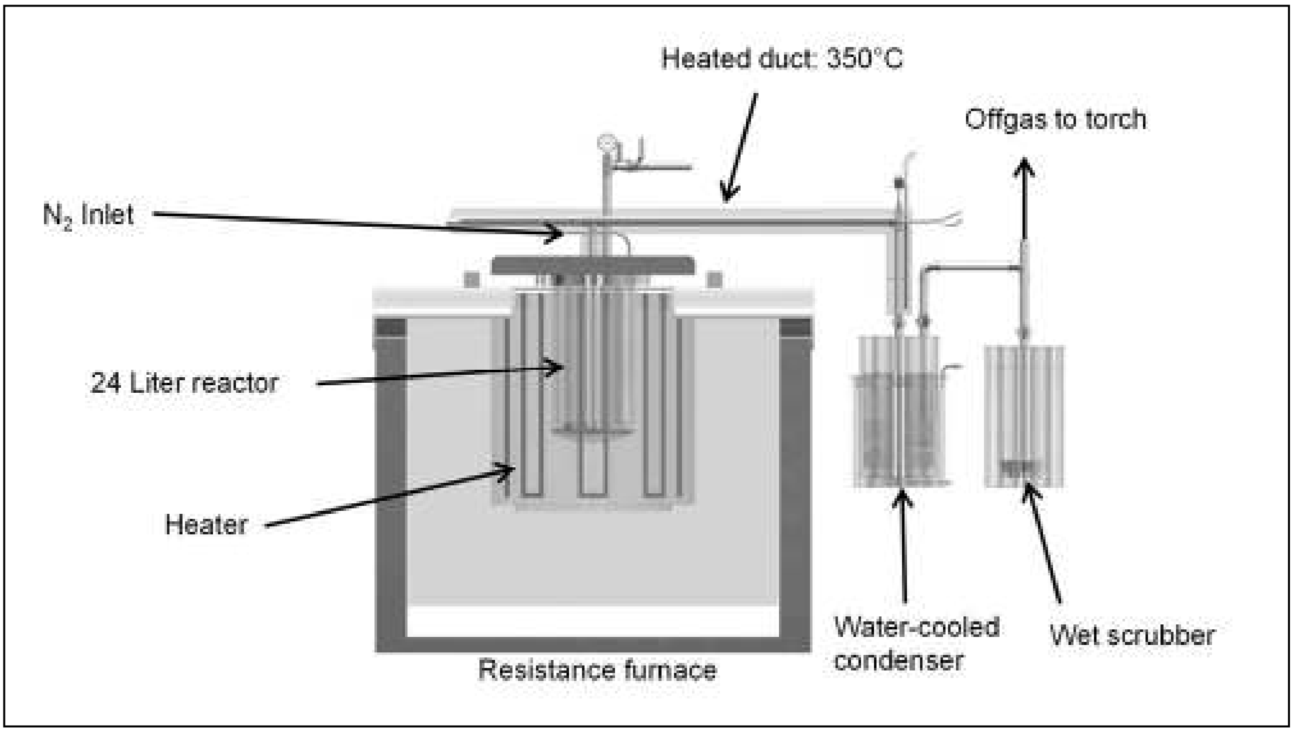

Figure 4: Setup for pyrolysis

3.2 Mechanical Treatment and Chemical Analysis

Pyrolysis was followd by a mechanical treatment according to the two mentioned routes. The concept of route 1 was the avoidance of a further comminution step and the idea that gallium can be concentrated in a certain fraction only by direct sieving of the pyrolysis residue. For the separation a shaking sieve was used which was equipped with mesh sizes between 10 mm and 90 µm (see Figure 2). Components much bigger than 10 mm, were picked out by hand. Due to the brittleness of the pyrolysis residue, it was assumed that the impact, originating from the vibrations of the shaking sieve, could be sufficient to separate plastic-metal-composites.

In consideration of route 2, the procedure exhibits some modifications which were based on the results from route 1 to improve the gallium recovery. Therefore, an additional comminution of the pyrolysis residue using a ball mill was applied for 20 minutes to realize the formation of a higher amount of fines. The ball mill was made of a steel cylinder having a diameter and length of 30 cm. Inside the cylinder, 30 steel balls with a diameter of 4 cm and 100 balls with a diameter of 1 cm enabled sufficient impact on the input material. In terms of sieving, only one mesh size (500 µm) was used in the sieving step – beside hand picking of very large components.

Apart from large metallic components bigger than 10 mm, all sieve fractions were analyzed chemically to identify the distribution of gallium, but also the fate of some more elements, such as copper, gold silver, and rare earth elements. The chemical analysis was done by microwave pressure digestion in aqua regia and ICP-OES. Prior to the analysis, sieve fractions from route 1 and 2 larger than 90 µm were pulverized in a planetary ball mill.

4 Results and Discussion

4.1 Pyrolysis

Figure 5 depicts the appearance of one charge of crushed smartphones before and after pyrolysis. Obviously, a significant shrinking of the bulk volume has happened.

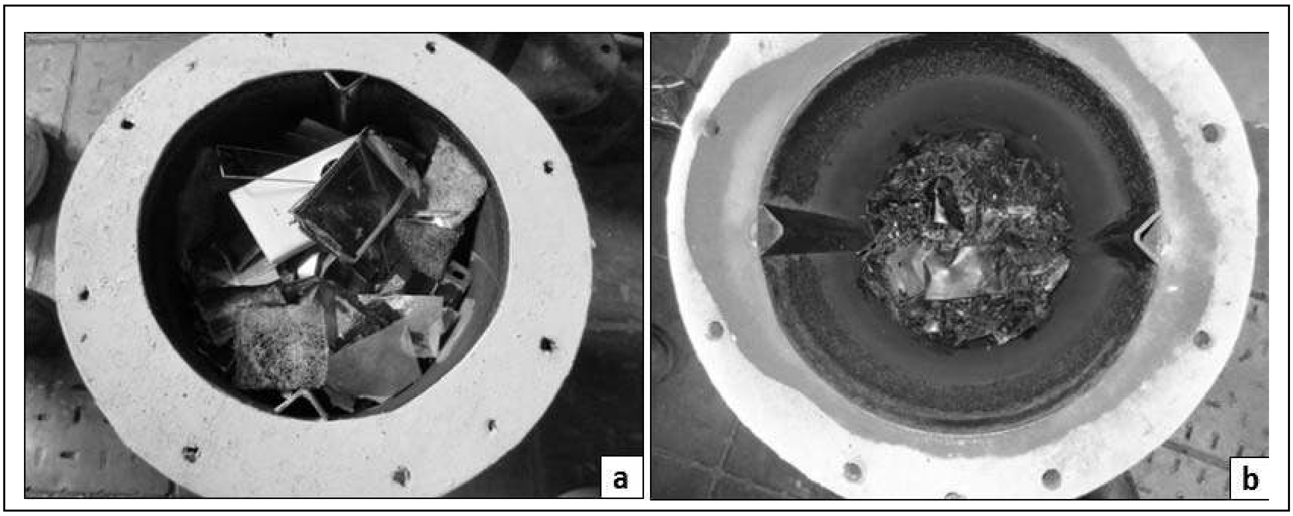

Figure 5: Smartphones in reactor before (a) and after (b) pyrolysis

Detailed mass losses of the several charges are listed in Table 2. For route 2 an overall mass loss was calculated, because all three charges were merged together between pyrolysis and ball milling. The differences between mass losses are due to the fact that the three charges had no equal composition, because the overall bulk of 13 kg was devided randomly after crushing. However, there is still a difference of 3 % in the mass loss of route 1 (28 %) and the overall loss in route 2 (25 %) which can be explained with the smartphones' variety in type and year of manufacturing. Hence, the charges of route 1 and 2 exhibit slight differences in composition, but the importance of this inaccuracy is marginal for the further work, because it does not affect the distribution of single elements during mechanical processing.

Table 2: Mass loss of crushed smartphones during pyrolysis

	Route 1	Route 2
Charge 1	28 %	24 %
Charge 2		31 %
Charge 3		17 %
Overall	28 %	25 %

5.2 Mechanical Treatment and Chemical Analysis

Figure 6 represents the results from direct sieving during route 1. The left diagram depicts the weight percent and the gallium content in every sieve fraction. Apparently, a significant Ga enrichment of 120 ppm could be achieved in the fraction having a grain size between 1 and 5 mm, whereas the concentration of the other fractions varies between 15 and 27 ppm.

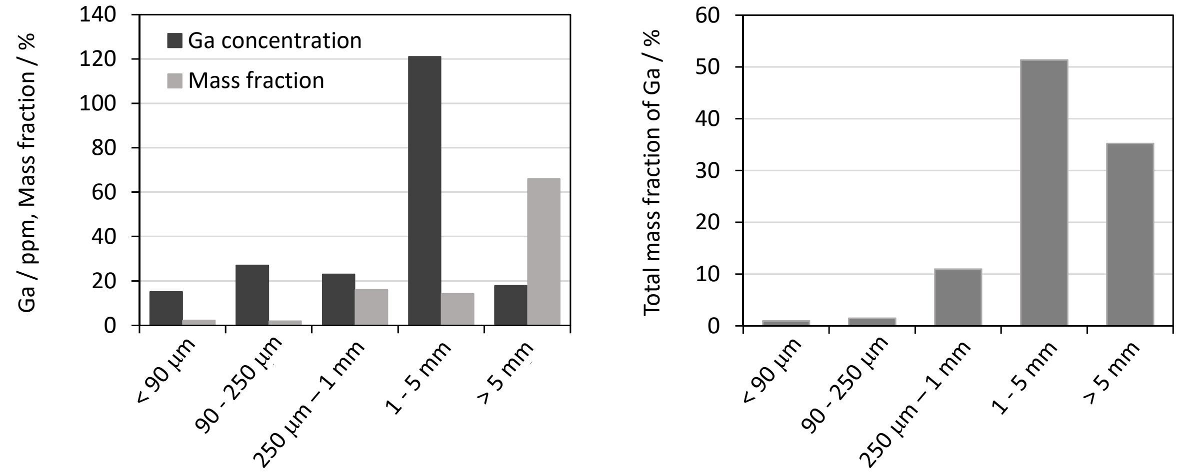

Figure 6: left: Ga concentration and mass fraction of every sieve fraction of route 1; right: Dissipation of total Ga over sieve fractions

However, it has to be considered, that the portion of fraction 1-5 mm is much lower compared to fraction > 5 mm, which has a considerable influence on the absolute amount of Ga in every sieve fraction. This fact is regarded in the right diagram of Figure 6 which shows the dissipation of total gallium in the 4.5 kg-charge of smartphones. According to the columns, only 51 % of total gallium ended up in fraction 1-5 mm. Because of the high mass percentage, 35 % of total gallium were collected in fraction > 5 mm and another 10 % of Ga accumulated in fraction 250 µm-1 mm. On the one hand these data reveal that it is possible to produce a sieve fraction having a high concentration of gallium, but on the other hand, the gallium yield of this fraction is lowered by its low mass percentage related to the other sieve fractions. Referring to the process concept of route 1, it can be concluded that most Ga-bearing ICs still adhere to the printed circuit boards after sieving and could not be released (see Figure 7, left picture).

Consequently, it was decided to modify route 1 according to route 2 which means that the pyrolyzed smartphones were treated in a ball mill as described before. The outcome of this procedure can be obtained from Table 2.

Table 2: Mass loss of crushed smartphones during pyrolysis

	Mass fraction [%]	Ga [ppm]
< 500 µm	44.5	139
> 500 µm	55.5	0

As expected, the ball milling highly increased the proportion of the fines < 500 µm up to 44.5 %. Furthermore, the Ga concentration in this fraction was 139 ppm. Because the coarse fraction > 500 µm consisted of metals and glass fibers only and all PCBs were free of any ICs (see Figure 7, middle picture), it can be assumed that all the gallium from the input material went into the fines.

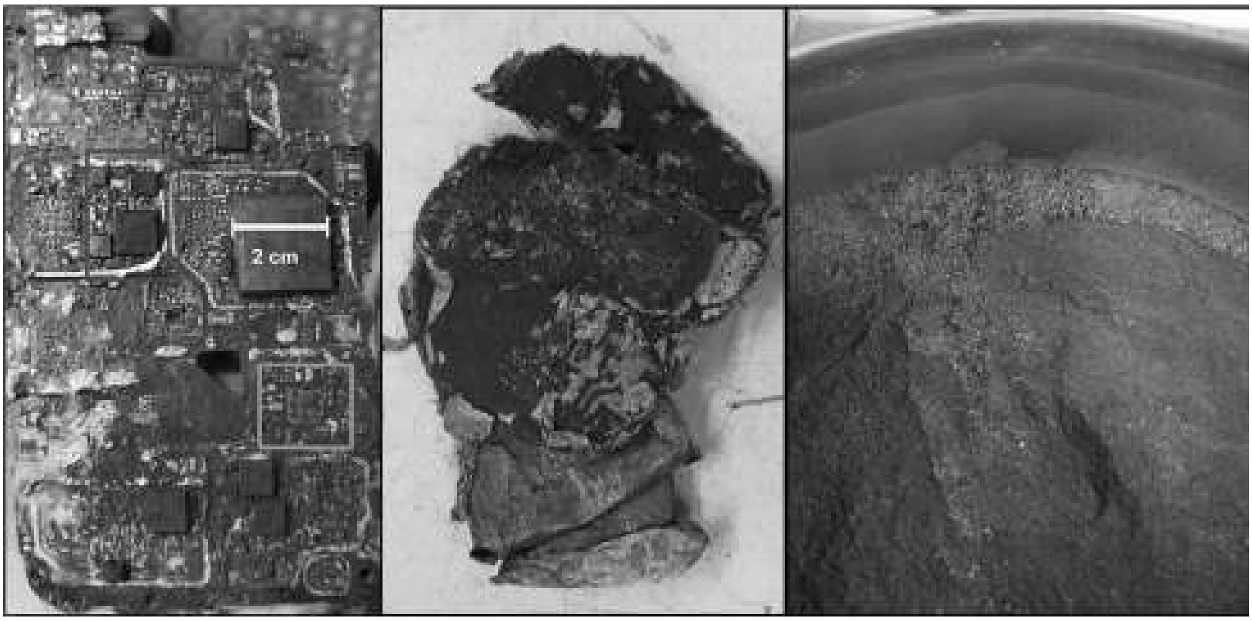

Figure 7: PCB after pyrolysis and direct sieving (left); PCB after ball milling (middle); fines < 500 µm (right)

A detailed survey of other (valuable) elements detected in the fines is given in Figure 8. Apart from Ga, a significant enrichment of Au, Nd and Dy has happened. If the Au concentration in the fines is related to the results of Holgersson et al. [14] it can be concluded, that all the gold from the PCBs must have ended up in the fines as well.

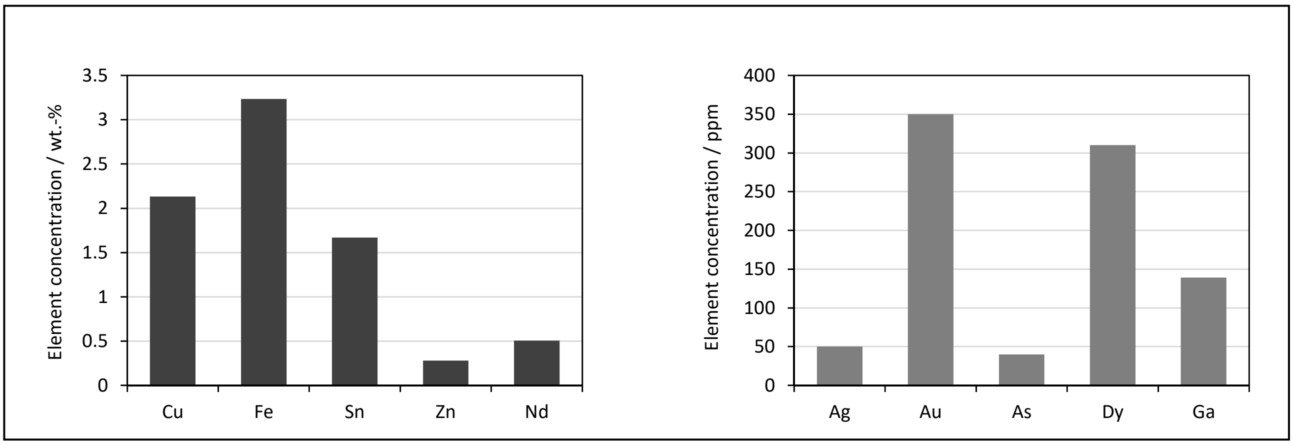

Figure 8: Elemental composition of fines (< 500 µm) after ball milling and sieving

Compared to the gold concentrations on a single PCB, however, gold was diluted from ~1000 ppm to 350 ppm during route 2 due to the fact, that lots of particles originating from other parts of the smartphones accumulated in the fines. This results in a dilution factor of 2.8 for the case that the PCBs exhibit an average gold concentration of 1000 ppm. After applying this factor to the Ga concentration of 139 ppm in the fines, a Ga content of 389 ppm on the untreated PCB follows. In contrast to the literature, this value appears to be very high, but at this point it has to be taken into account that all calculated numbers are based on average values and estimations obtained from different works so that a certain error has to be accepted. Regarding platinum group metals in this study, all results from ICP-OES were below the detection limit. Results for Ag and As have to be considered critically, because these particular elements behave very inconsistent during a series of several analysis. Here, the major source of error seems to be the microwave pressure digestion in aqua regia. Especially the concentration of Ag is expected to be much more higher than indicated Figure 8.

Finally, a good benchmark for the concentration of Ga can be done by comparing the value from the fines with other primary and secondary Ga sources as depicted Figure 9. It becomes evident that the gallium content of the fines is at least 75 % higher compared to other raw materials. Therefore, the fines obtained from pyrolyzed smartphones appear to be a potential raw material for the recovery of gallium, but also for gold and rare earth elements.

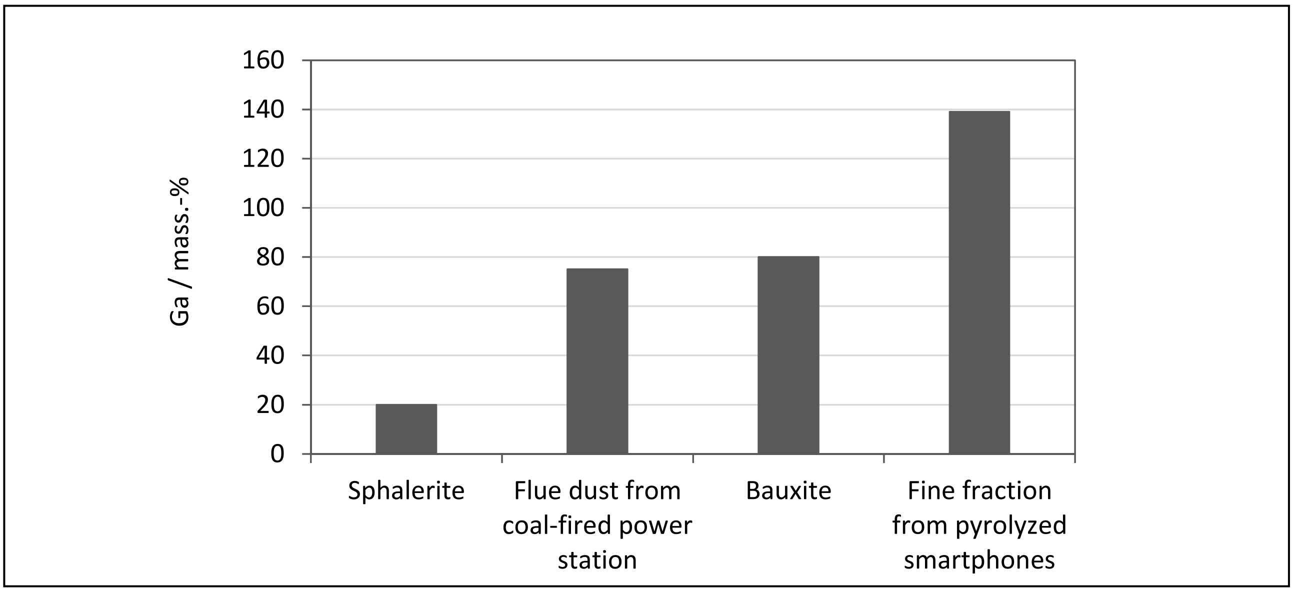

Figure 9: Comparison of different primary and secondary Ga sources: Sphalerite [15], flue dust from coal-fired power stations [16] and bauxite [17]

5.3 Metallurgical Assessment

After thermal and mechanical treatment, the point of interest is the metallurgical treatment of the pyrolysis products from route 2. The coarse fraction > 500 µm is suitable for further mechanical separation of non-metals, iron and non-ferrous metals which can be introduced into their specific production routes. Concerning the fines, however, a direct metallurgical processing seems to be appropriate due to the low grain size and the high variety of elements. Regarding copper and precious metals, straightforward pyrometallurgical smelting would be the process of choice. In this case, carbon and silica can act as fuel / reduction agent and slag former. But as already mentioned above, such a procedure would cause the loss of gallium and all other ignoble trace metals. Hence, a selective extraction of gallium prior to smelting has to be achieved which can be realized most likely by hydrometallurgical processing. Due to its amphoteric character, Ga can be dissolved in acidic as well as in basic solutions, particularly at $pH < 3$ or $pH > 12$. In both cases, a high solution potential (= oxidizing conditions) is required to dissolve Ga from the GaAs matrix [18, 19]. Aiming for a selective process, most acids – specially common mineral acids such as HCl, H_2SO_4 and HNO_3 – do not come into consideration, because they are able to dissolve greater amounts of Cu, Ni, Zn, Sn, Fe and Ag which are not favoured to be coextracted. Liu et al. reported that oxalic acid can be used for a selective dissolution of Ga [20]. However, it has to be regarded that this study was focused on the treatment of zinc refinery residues which contain Ga in its oxidic state. Because oxalic acid acts as a reducing agent, a simultaneous oxidation of Ga would not be reasonable. On the other side, oxidative alkaline leaching using NaOH seems to be an appropriate method as suggested by Wang et al.[21]. Although NaOH dissolves Al and Si, other elements such as Fe, Cu and precious metals are poorly or not attacked. A further benefit of NaOH as leaching agent is the already existing technology for final extraction of Ga from the alkaline liquor. If such a liquor is obtained, it can be introduced into the route of Ga extraction from bauxite [9]. A detailed elaboration of hydrometallurgical Ga extraction from the fine pyrolysis residue is conducted in part II of this work.

The leaching residue, still rich of C, Cu, Nd and precious metals, can be further treatened pyrometallurgically via reductive smelting and selective oxidation so that Cu and precious metals are collected in the metal phase whereas Nd and Dy are oxidized and pushed into the slag. Subsequently, hydrometallurgical treatment of the slag allows the recovery of REE. Figure 10 illustrates the whole process chain including thermal / mechanical pretreatment and metallurgical processing. Here, the process steps for the recovery of Cu, Au, Ag and REE are highlighted by a box with a broken frame, because these steps are not intended in this work and rather a matter of theoretic consideration. Especially the hydrometallurgical recovery of REE has to be considered critically in terms of economic aspects.

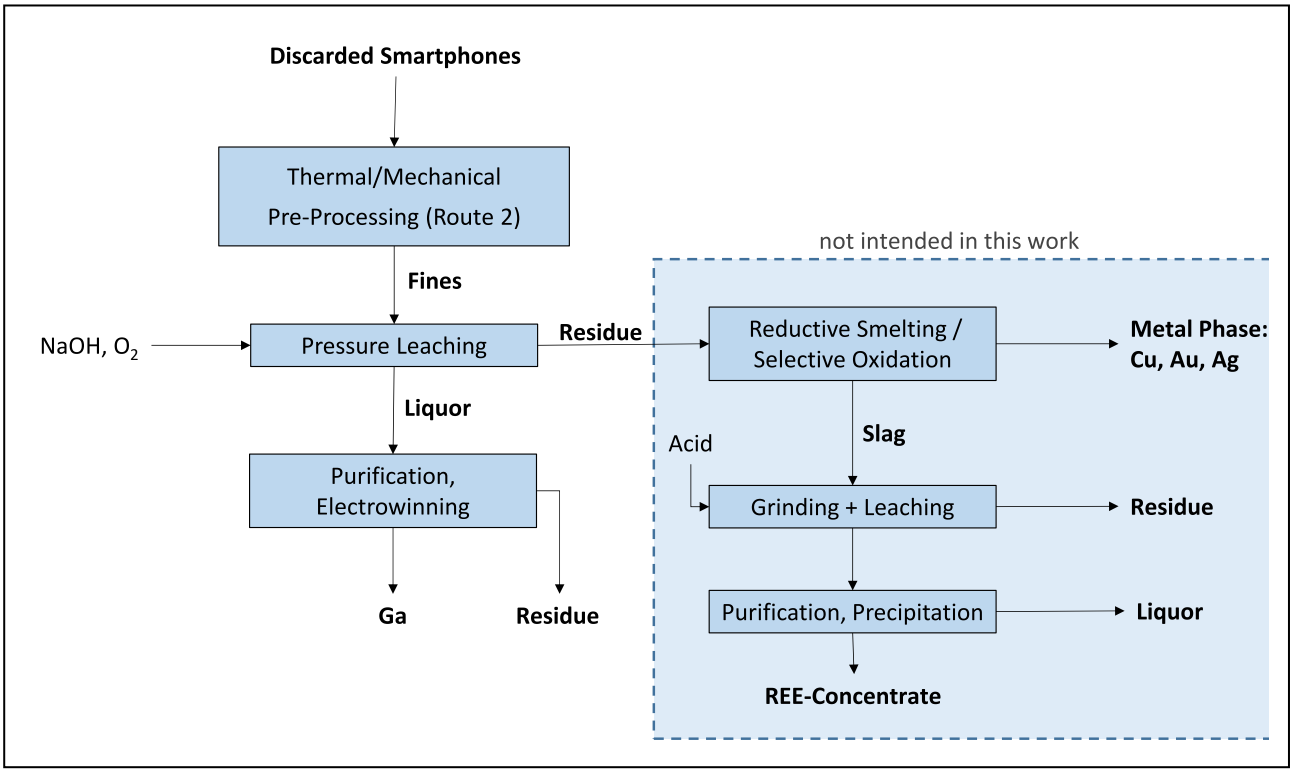

Figure 10: Possible metallurgical treatment of fines obtained from pyrolysis and mechanical treatment

5 Conclusion

It was shown that the combination of thermal and mechanical pretreatment of used smartphones via pyrolysis and milling / sieving is a smart way to produce a fine intermediate product which exhibits a considerable Ga concentration of 139 ppm. Additionally, Nd, Dy and Au were enriched as well and it can be assumed, that the whole amount of mentioned metals - including Ga - ended up in the fines. It was found further that ball milling is a necessary step to remove remaining GaAs compounds from PCBs. However, the results of chemical analysis and the review of latest literature make clear that an accurate determination of metal yields and recovery rates is limited by a lack of knowledge on the exact initial composition of the input material. The latter is not constant and varies according to the smartphones' type and year of production. For a selective Ga recovery from the fines, hydrometallurgical processing comprising oxidative leaching with NaOH followed by purification and electrowinning is suggested. Cu, Au, Ag and REE can be separated stepwise from the leaching residue applying pyro- and hydrometallurgical procedures. Finally, the outlined process should not be limited to the processing of smartphones only, because it also can be applied on other complex materials which occur in much greater amounts like waste printed circuit boards. In general, the results show how the issue of metal-bearing composites can be solved and where single metals end up during such a process.

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