The possibilities of hydrometallurgical treatment of discarded mobile phones

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ABSTRACT: This article deals with possibilities of selective leaching of discarded mobile phones. The preparatory part was focused on mechanical pre-treatment and the aim of the next part was to confirm or refute necessity of leaching different granulometric fractions of discarded mobile phones separately. Diluted sulphur acid and temperature 60°C was used for leaching. Copper and zinc extraction were evaluated by AAS method.

1. INTRODUCTION

Mobile phones (MPs) use two billions people in the world [1]. In fact, most users upgrade mobiles at average two years and so the amount of MPs has been still grooving. In the year 2009 were nine million activated users of MPs in Slovakia (data source from annual report of three Slovak operators). It represents 531t batteries, 396 t metals and plastic. Material composition of MPs is as follows: precious metals (Au, Ag, Pd,..), base and specials metals (Cu, Ni, Co, Sn, Al, Fe, In, Bi,...), metals of concern (Be, Pd, Cd, As, Sb, Cr,..), halogens (Br, F, Cl,..), glass and combustibles (plastic). The metals of economic interest and environmental concern are primarily located in the electronic circuitry in the handset [2]. Compared to natural ores the valuable metals are concentrated in mobile phones many times more, for example: Au 1000 and Cu 10 times more. Considering these realities and fact, that rich ore fields are partially used up, these quantities of discarded mobile phones should to consider as secondary raw material. On the other hand, mobile phones also contain hazardous substances. Their uncontrolled dumping should cause negative impact on environment.

2. POSSIBILITIES RECYCLING OF MOBILE PHONES

Methods of metals recovery from mobile phones as a kind of WEEE are pyrometallurgical and hydrometallurgical. Both of these methods have advantages and disadvantages.

Pyrometallurgy (thermal methods, dry methods):
Using thermal energy and chemical or metallurgical properties of substances to melt down secondary materials in order to concentrate target metals for further processing and separate non-target substances into slag and/or volatile phase (example: IsaSmelt furnace, blast furnace, converter, calcinations...)
The advantages of process are relative easy and low-cost, suitable for heterogeneous materials. The disadvantages of process are mainly environmental impact and high investment cost.

Hydrometallurgy (wet methods):
Using acid and alkaline solutions at normal conditions and pressure and chemical properties of substances to separate target from non-target substances trough solution and leaching residues (example: cyanide leaching of Au, electro winning of Cu, precipitation, cementation, solvent extraction, ...) [2,3].
The advantages of process are using cheap, selective and removable leaching agents and easy plant. The disadvantages are: homogenous input materials, sewerage water with solid rests

Mechanical treatment is important before both of methods especially in hydrometallurgy. Batteries must be removed before mechanical or pyrometallurgical processing and special treated. Mechanical separation includes coarse shredding and further size reduction and separation techniques. The most common separation techniques used for secondary row materials is magnetic separation. Moving electromagnetic fields ECS are used to separate aluminium from others material.

2.1. *Pyrometallurgical treatment*

Umicore has recently completed mayor investments at its Hoboken plan, where besides precious metals and copper a large variety of base and specials metals are recovered. The plant has been developed to the globally most advanced full-scale processor of various precious metals containing secondary raw materials such as automotive catalysts and electronic – scrap, generating optimum metal yields at increased productivity. Fig.[2]

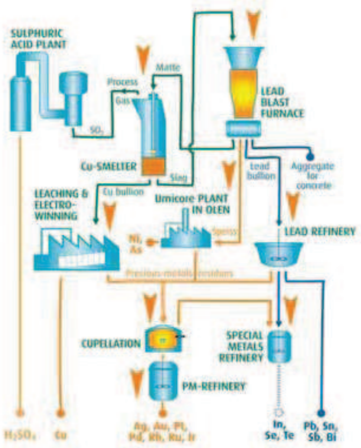


Fig.1 Flowsheet of Umicore's integrated smelter at Antwerp/Belgium [2]

2.2. *Hydrometallurgical treatment*

The basic operation in hydrometallurgical treatment is leaching. Many authors had concerned with leaching of electric or electronic waste (WEEE).

Tomášek at al. [5] leached the separated electric scrap in the laboratory scale. It was mainly represented by various types of contacts with Au 1 wt.% and Cu 75-85 wt. %. Three leaching solutions were tested on the extraction efficiency of gold. As a leaching solution were mixtures of inorganic acids, aqueous solution of thiourea and aqua regia used. Conditions of leaching were: ratio L: S=10:1, leaching time 300 minutes and 23°C without agitation. The best results were by using aqua regia (97,74% Au). In the next step was obtained gold with 99,99 % purity by Au-electrolysis.

Authors [6,7] treated three type samples of pre-treated mobile phones (MTs) without batteries, basic crushed sample MTs, non magnetic fraction crushed MTs. Thermal pre-treated MT at 900°C, air atmosphere during 3 minutes was heated.. These samples MTs in diluted hydrochloric acid and also diluted solution of ferric chloride acidified hydrochloric acid were leached. The ratio L:S 20:1and temperature 60°C, was used for each experiment. Leaching time was 90 minutes. Copper and silver efficiency was determined by AAS method. Using of ferric chloride as an oxidant medium caused higher copper and silver efficiency then using non oxidant hydrochloric acid. Pre-treatment sample MT by magnetic separation was not indicated significant influence on copper leaching. The thermal pre-treatment has positive effect on copper extraction.

For leaching experiments [8] were used whole and crushed printed wiring boards (PWBs). Reagents were sodium chloride and copper (II) chloride-2-hydrate. Solution was purged using oxygen. The optimal pH was between 1,5-2,5 and temperature 90°C during 7,5 hours. The effect of ozone (with concentration 3 vol.%) was also studied on a whole PWB into a glass cell containing tap water, the leaching time was 15 hours. Copper extraction was 45 mgCu /kg of ssrap. The effect of ozone was not significant influence on leaching.

Ving Hung Ha at al. [9] studied leaching of gold from the printed circuit boards (PCBs) of waste mobile phones. An effective and less hazardous system, a copper-ammonia-thiosulphate solution, as an alternative to the conventional and toxic cyanide of gold was used. 90% of gold from the PCBs samples, was leached out by using a solution containing 20mM copper, 0,12 M thiosulphate and 0,2 M ammonia, during 10 hours.

The conclusion as follows that hydrometallurgical treatment discarded mobile phones should be a method for recovering metals from WEEE. The aim of this article is possibilities of selective leaching of mechanical pre-treated fractions mobile phones. These experiments are considered as base input experiments.

3. EXPERIMENTAL

3.1. Characterisation of materials

Ten kilograms collected mobile phoned were used for the experiments. Mobile phones without hand removal batteries were mechanical separated by crushing on fraction -8+0 mm, by the hammer crusher (type RT15315) and then were homogenized. Homogenous sample was needed to prepare for leaching. The sample was prepared as follows.
The obtained bulk sample was quartering and a part of it was grinding by the vibrating mill (type RE4575. By reason of the more accurately it was obtained two analytical samples MT1 and MT2 assigned for chemical analysis. The samples were dissoluted in aqua regia and determined by AAS method (Varian Spectrophotometer AA20+). The chemical composition samples MT1 and MT2 are shown from Tab. 1. The scheme of mobile phone sampling is shown on Fig.2. The majority of the metal in mobile phones is copper.

Grain size analysis of crushed mobile phones was done, a one hundred grams of sample (M1) fraction -8 + 0 mm, were used. The sieve size was 8; 4; 1; 0,71; 0,4 mm and screening time was 15 minutes. Results are represented by cumulative on the Fig.3.

Tab. 1: Chemical analysis of two representative samples of mobile phones M1 a M2 in wt. %

wt.%	Cu	Fe	Ni	Sn	Pb	Zn	Al	Au	Ag	Pt
MT1	13,13	3,61	1,7	1,25	0,47	2,26	0,87	0,1	0,21	0
MT2	14,32	1,67	0,92	2,04	0,61	0,49	1	0,09	0,22	0

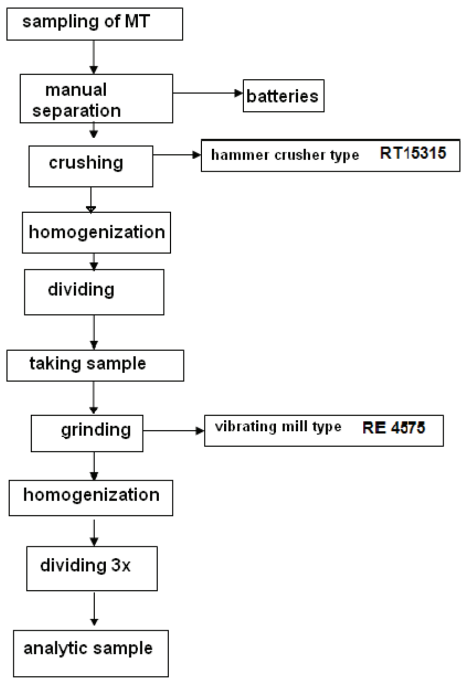


Fig. 2: The scheme of mobile phones sampling

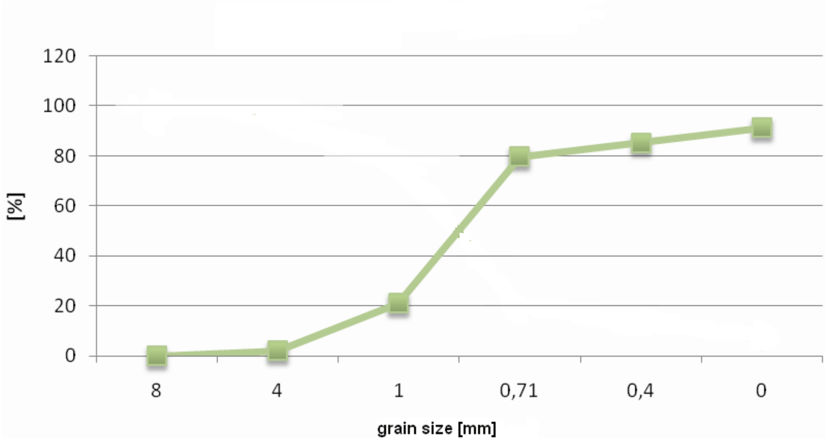


Fig. 3: Grading analysis of sample M1 (cumulative curve)

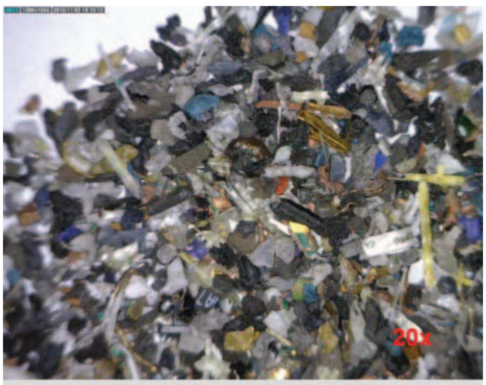
3.2. Leaching

The experiments on three fractions <-4+1>, < -1+0,7>, <-0,7+ 0,4> mm, and the whole fraction < -8+0> mm as well, were carried out. The chemical composition of fractions was determined by AAS method seen on Tab.2. Every samples fractions by optical microscopy on optic stereomicroscope (type Dino-Lite set 4.3 IM10283) were exposed of observation. Any optic filters were not used for analysis with 20 times magnification. The morphology of particles is shown on Fig.4.

Tab. 2: Chemical analysis of grain class of crushed mobile phones

mm / w.%	Cu	Fe	Ni	Sn	Pb	Zn	Al	Au	Ag	Pt
MT3 <-4+1>	8,88	25,66	8,72	0,63	8,14	1,08	0,64	0,042	0,059	0
MT4 <-1+0,7>	15,58	3,71	1,54	1,27	0,58	1,03	0,68	0,059	0,25	0
MT5 <-0,7+ 0,4>	21,68	2,55	1,54	2,80	1,34	0,65	0,83	0,051	0,086	0

The every fraction in 1M H_2SO_4 was leached during 60 minutes. The temperature 60°C and ratio L:S=50:1 was in all experiments. Leaching experiments were carried on apparatus showed on Fig. 5, Every 5, 10, 15, 30, 60 minutes 10 ml samples for chemical analysis was taken. Copper and zinc efficiency were evaluated by AAS method.



a) MT4 <-1+0.7 > mm

b) MT3 <-4+1> mm

c) MT5 <-0.7+0.4> mm

d) MT1 < -8+0 > mm

Fig. 4: The morphology of particles 20 x magnification

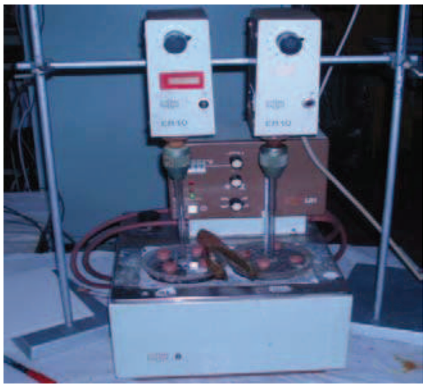


Fig. 5: Scheme of apparatus on conventional leaching

3.3. Results

Fig. 6 shows the comparison of kinetic leaching curves of zinc extraction on various fractions pre-treated mobile phones. The best zinc extraction was achieved 17 % after 20 minutes leaching on whole fraction -8+0 mm. The kinetic curves of three fractions have similar character however character of fraction -4+1mm is different. It is assumption that by continuation of leaching should by higher zinc extraction. In was supported that copper leaching occurs only in oxidizing medium as a showed on Fig. 7.

In comparison with the visual observation of surface morphology of sample a) MT 4 (Fig.4) before leaching and this same sample after leaching (Fig.8) can see changes on surface metals. It can be supported that material was leached,

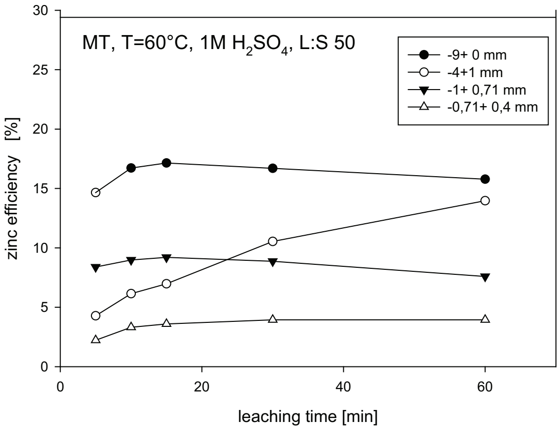


Fig.6: The comparison of kinetic leaching curves of zinc extraction on various fractions pre-treated MT

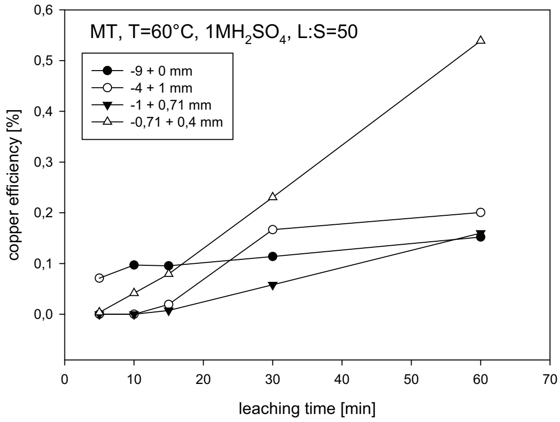
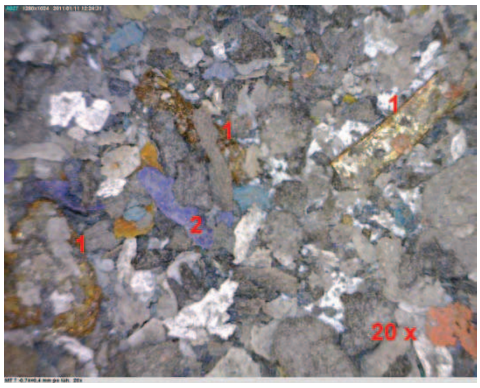


Fig.7: The comparison of kinetic leaching curves of copper extraction on various fractions pre-treated MT



MT 4 <-1+0.7> mm, after leaching

Fig. 8 Morphology of particles sample MT4 after leaching 1- changed metals surface

3. CONCLUSION

In this paper was studied possibility of hydrometallurgical leaching discarded mobile phones. These experiments are considered as input experiments. The granulometric fractions of mobile phones were leached in acid medium. The best zinc extraction was achieved on fraction -8+0 mm. From result follows that best way of treating of MPs is leaching non separate mobile phones on granulometric fraction. Achieved zinc extraction was only 17 % after 20 minutes leaching, however this amount is not sufficient for selective leaching. The reason can be low concentration or low temperature of leaching medium. Therefore is necessary to continue in next leaching experiments for recovering higher zinc extraction with the changing of leaching characteristic parameters. In the next step of hydrometallurgical treatment will be selectively leaching mobile phoned in the following way: 1- leaching in (H_2SO_4) => Zn recovery, 2- leaching in H_2SO_4 + Fe^{3+}=> Cu recovery and 3- leaching in (HCl + HNO_3) => Au recovery.

4. ACKNOWLEDGEMENT

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