COMPLEX CHARACTERIZATION OF THE METALLURGICAL SOLID WASTES FOR ALUMINOTHERMIC 4R APPROACH

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Aluminothermy is an emerging technology for metallurgical solid wastes recovery. Through ED(P)-XRFS, XRD, SDAR-OES, SEM and metallography were achieved data to establish the correlations among the waste characteristics, the technological variables, and the outcomes of the aluminothermic waste treatment. The paper provides valuable elemental and phase analytical results corroborated with SEM and metallographic observations. The achieved results demonstrate the adequacy of aluminothermy for EAF dust recovery, but for eradicating of the historic metallurgical waste dumps. The novelties addressed in the paper supports the aluminothermy as effective tool for the implementation of the Circular Economy Policy in Romania, but at EU level.

Keywords: metallurgical solid wastes, recovery, aluminothermy, iron oxides

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1. Introduction

The Circular Economy Policy of the European Commission (EC) lunched in 2015 has boosted systemic changes in designing the production processes as to lower their impact on environment [1]. Steel is at the centre of the circular economy [2]. In 2020, the EU published a Circular Economy Action Plan. This plan foresees closing the loop of the materials used in goods manufacturing, as to achieve zero waste. Also, the Closing the Loop Policy implies the waste transformation into resources. This task needs new technologies, processes, services, and business models for waste management. EC has predicted that research and innovation will be a major factor in encouraging the transition to the circular economy [1-3]. In this view, the European Steel Association (EUROFER) promotes technologies that are developed for efficient valorisation of solid wastes. EUROFER points out that a Green Deal on Steel should targeting a green steel industry in the period 2021 to 2030. This plan can help to promote new efficient technology for reducing CO_2 emission and for advanced utilization of solid waste in manufacture of conventional products, but also for conversion them into new products [4]. A part of the metallurgical solid wastes is reduced, reuse, recycle or restored (aka 4R), but another part is deposited in excavated land forming dumps. It is considered that approximately 60% mass of metallurgical solid wastes are dumped in less developed countries [5]. The Romanian steel industry has generated solid waste dumps in excavated land or even in open space that create air pollution in the form of dusts, flying ashes and subsoil pollution through levigates or leachate waters [5-6]. The Environmental Report for Romania's Energy Strategy 2020-2030, with the perspective of 2050 estimates that industrial solid waste dumps affect 844 ha, of which 360 ha are excessively affected, most being in counties with mining, steel industry and non-ferrous metallurgy [6]. Many solutions were tested for metallurgical waste valorisation through 4R approaches, mostly consisting in iron scrap collection, slag reuse as filler for road construction, inert waste used as brick filler and additives for porous building materials etc. [7-17]. The fine powdered fraction coming out from waste crushing and milling, EAF steelmaking etc., is further landfilled [7, 8]. Thus, an important fraction of the treated waste remains useless i.e., waste. In this view, aluminothermy is an emerging technology for solid waste valorisation, both material and energetic [18-25]. Aluminothermy is anticipated as the basic process for an efficient technology for recovering the powdered solid wastes that contain significant quantities of iron oxides [18, 19].

On the other hand, any 4R technology depends on waste characteristics i.e., elemental and phase compositions, granulation, humidity, useless fraction (soil, sand, organic matter) [26, 27]. The use of the aluminothermic reaction in the treatment of steel industry by-products critical depends on the waste elemental

and phase compositions [21, 23]. Accordingly, the first stage of an aluminothermic technology development for metallurgical solid waste valorisation consists in waste characterization. The exactness of the analytical outcomes is of critical importance for the proper dosing of the aluminothermic reactants (oxidizer, reducer, inhibitor, pre-alloys). The powdered metallurgical waste characterization implies a method budget that must contain at least: XRF for elemental analysis, XRD for phase analysis, LOI for measurement of humidity, organic mass, and equivalent calcium carbonate content, optical and SEM (EDAX) for particle morphology observation, eventually for size and specific surface estimation, granulometric analysis [27-29].

2. Specificity of the aluminothermic process applied to solid metallurgical wastes bearing iron oxides

The aluminothermy is a well-known technique used for rail track welding [30]. The rail track welding uses a thermit kit made of a mixture of natural or synthetic iron oxides together with aluminium powder as reducing agent, a carbon source, and a flux [30]. The ferrous oxide (Fe_3O_4), the ferrous-ferric oxide (Fe_2O_3), and the ferric oxide (FeO), aka magnetite, hematite and wüstite, are used in different proportions, to achieve the desire heat and steel quantities. Unlike the magnetite and hematite, the wüstite, has a variable composition close to FeO (23.10 %, $Fe_{0.85}O$ ÷ 25.10 %, $Fe_{0.95}O$) [18,30]. All compositions given in this paper are weight percentage (%wt). The aluminothermic yield strongly depends on the iron oxide type as is shown below [18, 21, 30]:

$$3FeO + 2Al = Al_2O_3 + 3Fe + 693\,Kcal/kg \quad (1)$$

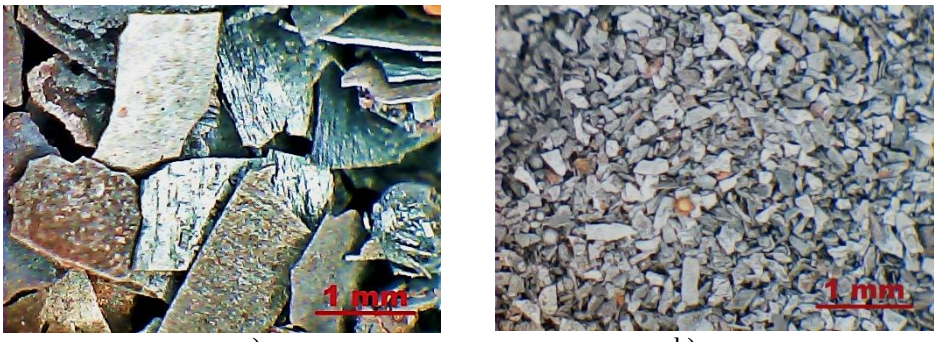
$$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe + 848\,Kcal/kg \quad (2)$$

$$3Fe_3O_4 + 8Al = 4Al_2O_3 + 9Fe + 748\,Kcal/kg \quad (3)$$

The Eqs. (1-3), show that the heat yield of the FeO is lower than in cases of using magnetite or hematite. Therefore, an iron bearing waste must contain mainly magnetite and hematite to be proper for an aluminothermic treatment. Hence, XRD must be used for iron bearing waste characterization, as it is the most effective for such a purpose [31].

The mechanism of the reaction between iron oxide and Al depends on the particle size distributions for both reducer (Al) and oxidizer (iron oxide). Also, the aluminothermic reaction is hindered by the corundum shell of the Al particles. Therefore, it is important to control the Al particle size and the Al_xO_y shell thickness for enhancing the aluminothermic yield. Furthermore, the envisages waste for aluminothermic treatment consist of heterogeneous phases of iron oxides powder and lumps that may be embedded in other useless minerals or organic matter as it can be seen in the Fig. 1. Consequently, for a proper

exploitation of the ferrous waste, it is necessary to crush it, followed by milling, as to obtain fine grained precursor. In case where the waste contains humidity and organics then it must be calcinated at 800-1000 ^{o}C. But any supplementary preparation of waste implies additional costs which may compromise a recovery technology. Fortunately, by a proper design, the great amount of heat generated by the aluminothermic reactions can be used to dry and calcinate the waste, to generate the electricity needed to crush and to mill the waste. Thus, the 4R based on aluminothermy seems being the best solution for the removal of the historical metallurgical dumps and to rehabilitate the land field.



a) b)

Fig. 1 Optical microscope images of iron bearing waste

In such circumstances, the development of an aluminothermic technology for metallurgical solid waste recovery needs a budget of testing methods and adequate equipment as to ensure a holistic characterization of the addressed waste. The holistic characterization aims a proper set up of the technological parameters depending on waste properties. The literature and our experience in the field indicate two class of testing methods:

a) powder testing methods (granulometry by sieving or laser measurement, humidity measurement, organic content measurement, calcite content measurement)

b) physic-chemical methods (chemical analysis by ED(P)-XRFS, phase analysis by XRD; morphological analysis by optical and electron microscopy).

The paper addresses the physic-chemical methods and emphasises the specificity of these methods when they are applied to ferrous waste that will be subjected to aluminothermic treatment.

3. MATERIALS AND METHODS

The paper addresses the complex characterization of 3 sorts of metallurgical wastes. Two sorts are primary sampled from two huge historical dumps in Romania whose identities are kept anonymous from legal reasons. The

third one is an electric arc furnace (EAF) dust. The sampled increments were comminuted and sorted using an magnetic-drum separator to obtain an iron enriched waste fraction. All the laboratory sub-samples were dried at 105-110 ^{o}C for 6h. The wastes were investigated by ED(P)-XRF spectroscopy, X-ray diffraction (XRD) and SEM microscopy. The XRFS was chose as it is the most suitable technique for measurement of the elements and oxides composition of a waste. An ED(P) Xepos spectrometer, AMETEK, was used to measure the chemical compositions of the specimens. This equipment has a large analytical range (Na-U), is faster and needs simple sample preparation. The Xepos has the advantage of lowering the level of the background fluorescence radiation through polarizing the exciting X-ray by the secondary targets [31]. The Xepos uses 3 X-ray fluorescence spectra (Fig. 2) for a better assessing of the elemental concentrations. The way in which XRFS quantifies the iron oxide is a drawback as all the Fe content is assigned to Fe_2O_3, even that Fe can be incorporated in Fe_3O_4, FeO, Fe_2Si etc. To discriminate the phases into which the Fe is incorporated it is needed to perform XRD analysis. The XRD analyses were conducted using a Panalytical X'Pert PRO MPD X-ray diffractometer with high-intensity Cu–Kα radiation (λ = 1.54065 Å) and 2θ ranging from 10° to 90°, with a 0.002^{o} step. The qualitative and quantitative XRD analyses aim identifying and quantifying the phases and their mass ratios into the waste under investigation.
The kinetic and velocity of an aluminothermic reaction depends on the particle size and shape of the iron oxide as the redox reactions occur at the atomic scale. Thus, as the surface area is larger as the sites favourite the occurrences of the redox reactions. SEM microscopy can provide information on the shape and size of particles even on the size distribution. The morphology and particle size investigations were conducted via SEM observations using a QUANTA INSPECT_F microscope, with a field emission gun. The main expected products of the aluminothermic reactions are steel or cast-iron lumps. Optical emission spectrometry and microstructural investigation were used to assess where the lumps are steel or cast-iron. The elemental compositions of the iron lumps were measured with a Spark Discharge in Argon-Optical Emission Spectrometer, SpectromaxX, AMETEK, while a Reichert UnivaR metallographic microscope was used to observe the microstructures of the iron lumps.
The outcomes of the above tests were used to dose the aluminothermic reactants i.e. aluminium reducer, iron oxides and inhibitor and to establish the nature of the products of the aluminothermic reactions.

4. RESULTS AND DISCUSSIONS

The waste studied specimens were denoted as follows: IOW1; IOW2 and IOW3. Also, there were investigated the products of aluminothermic reactions

denoted as follows: P-IOW_1; P-IOW_2 and P-IOW_3. The calculated oxide composition of the specimens is given in table 1. The ED(P)-XRFS oxide compositions of the IOW_1 and of the IOW_2 slightly differ when considering the main oxides as Na_2O, Al_2O_3, CaO, CuO i.e. with less than 3% wt., but strongly differ when looking at Fe_2O_3 and ZnO oxides i.e. greater than 10% wt. Thus, IOW_1 and IOW_2 wastes are very well fitted for aluminothermic recovery as they have over 84% Fe_2O_3, they do not contain many quantities of inhibitors Al_2O_3, SiO_2 and CaO <3%wt and the contents of hazardous elements (Cl, As, Cd, Cs, Hg, Pb, U) are insignificant.

Table 1.

ED(P)-XRFS compositions of the concentrated iron oxide wastes, denoted IOW1, IOW2 and IOW3.

Element	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	Cl	K_2O	CaO	Fe_2O_3	ZnO	As_2O_3	PbO
IOW_1	-	0.23	0.57	2.97	0.01	0.03	-	1.23	91.62	0.02	0.002	-
IOW_2	1.92	0.45	2.69	3.45	0.10	0.09	0.18	0.67	84.86	0.06	0.006	0.006
IOW_3	1.96	4.98	0.76	0.15	2.61	2.16	1.91	5.38	51.27	19.33	0.003	1.830
U(95%)*	0.04	0.08	0.06	0.04	0.04	0.08	0.10	0.60	0.08	0.12	0.002	0.006

** U(95%) is the expanded uncertainty with 95% confidence level*

The oxide composition of the IOW_3 specimen differs in a significant way from that of IOW_1, IOW_2 as it contains a smaller fraction of Fe_2O_3 (51.17%) compared to that of IOW_1 and IOW_2 wastes (91,62% and 84.86% respectively) (Table 1). ZnO concentration of IOW_3 (19.35%) is much higher compared to that of IOW_1 and IOW_2 wastes (0.02% and 0.06% respectively). Also, IOW_3 contains significant quantities of oxides as MgO, MnO and CaO compared to ones into IOW_1 and IOW_2 wastes. Besides, IOW_3 contains PbO which could cause environmental pollution during aluminothermic process if it is not retained from hot flue gases. Due to its specific composition the IOW_3, which is an EAF dust, can be subjected to an aluminothermic recovering process, but it needs a proper design as to prevent the emission of Zn and Pb vapours into atmosphere through hot flue gasses ejected during aluminothermic reactions.

The ED(P)-XRFS oxide composition depicts an approximative picture about the useful and detrimental contents of a powdered waste, but for a better designing of the aluminothermic process a XRD oxide analysis is needed to find out the allotropic ratios of iron oxides.

As could be seen in Fig. 2 the IOW_1 contains not only hematite, but magnetite as major phase (75%) while hematite content is only 19%. Also, *Ca* and *Si* are not incorporated in *CaO* an *SiO_2* as XRFS analysis let understanding, but in $CaSi_2$ (6%).

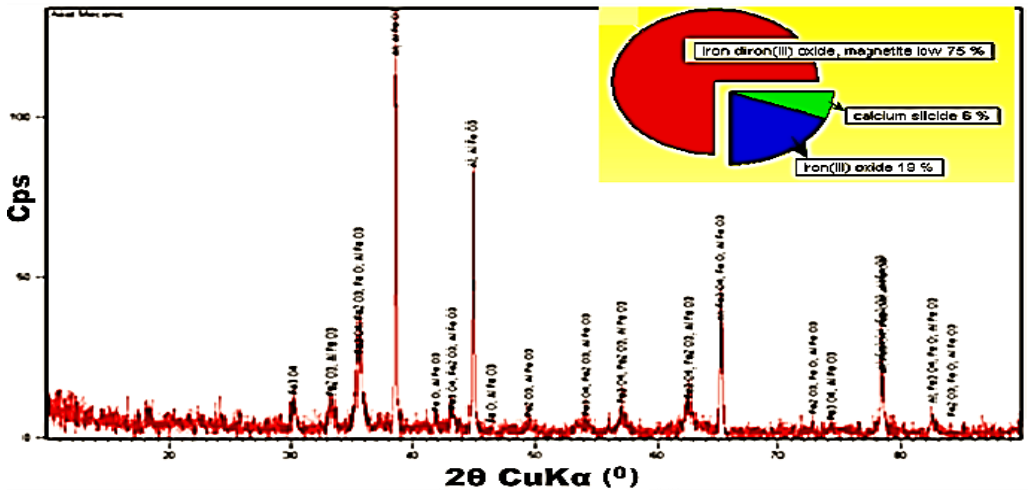


Fig. 2. The XRD pattern of the IOW_1 specimen ($\lambda_{Cu\ K\alpha}$)

The allotropic ratio into IOW_2 specimens is completely different compared to IOW_1 one as the hematite prevails (68%) compared to magnetite (16%) and wustite (6%) as is depicted by the diffractogram shown in Fig. 3.

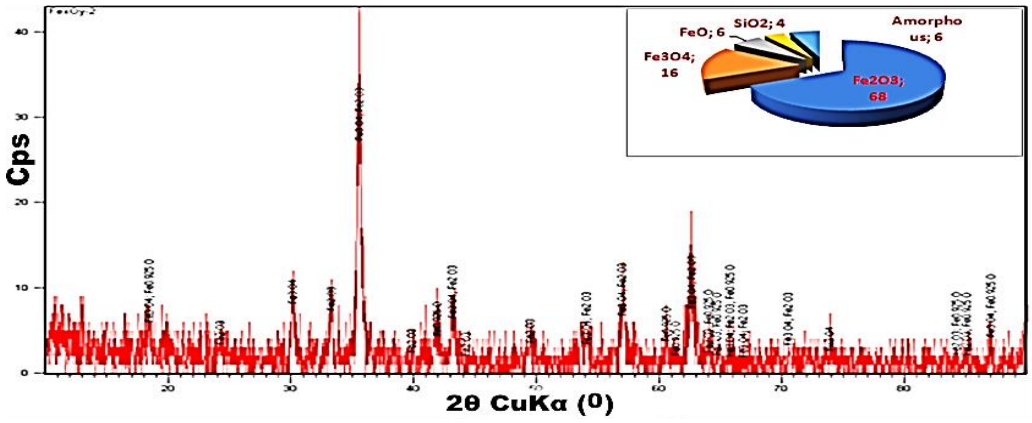


Fig. 3. The XRD pattern of the IOW_2 specimen ($\lambda_{Cu\ K\alpha}$)

The specific composition of the IOW_3 dust has imposed a more carefully XRD investigation using the $Mo_{K\alpha}$ radiation as to avoid parasitic effect caused by iron fluorescence and to extend the interplanar distance range. The diffractogram obtained on IOW_3 specimen is shown in Fig. 4.

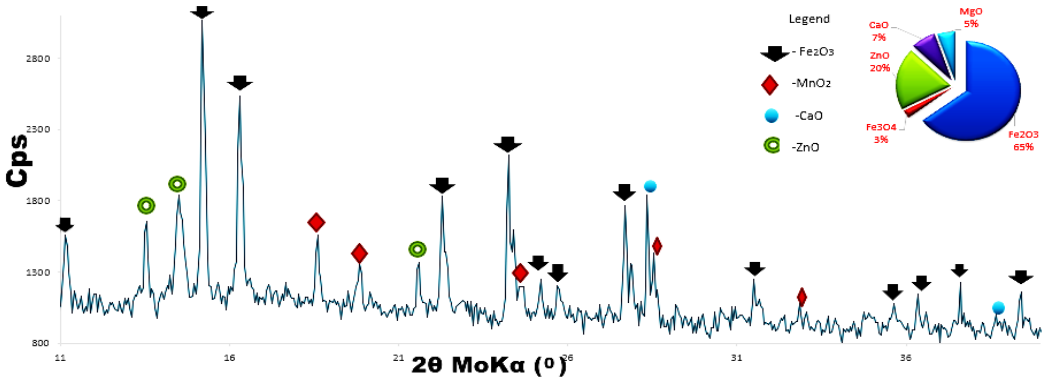


Fig 4. The XRD pattern of the IOW_3 specimen ($\lambda_{Mo\ K\alpha}$)

XRD analysis of IOW_3 shows up a great content of ZnO (20%) and CaO (7%) compared to IOW_1 and IOW_2. The MgO content (4%) occurs only in IOW_3, while SiO_2 and $CaSi_2$ were not identified in this specimen. Also, the EAF dust (IOW_3) contain mainly hematite and a small fraction of magnetite (3%) that indicates a smaller heat yield compared to IOW_1 precursor.

Fig. 5 depicts the morphological aspects of the powdered specimens under study after 1h ball milling, at different magnifications.

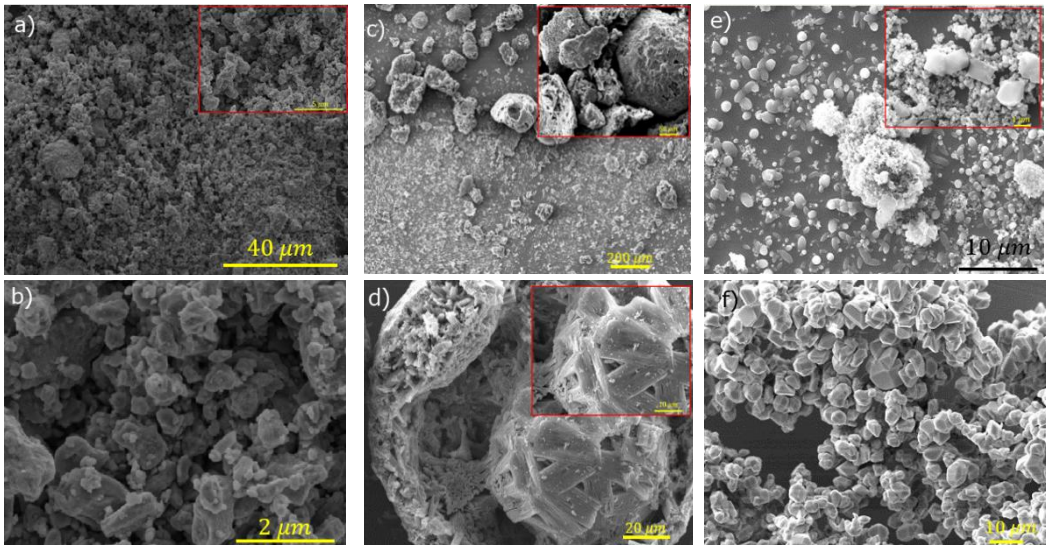


Fig 5. SEM images of the IOW_1 (a,b); IOW_2 (c,d) and IOW_3 (e,f)

The SEM images in Fig. 5 a, b shows up a broad distribution of the particle size of the IOW_1 waste. The particles have flat faces that seem being the result of the cleavage fracture during milling stage. The faceted shape (Fig. 1b) supports the crystalline structure of the magnetite particles as was confirmed by

XRD outcomes. The IOW_2 shows up particles with porous ovoidal shape (Fig.5. c). A closer look inside a particle reveals the substructure of the particle made of aggregated faceted crystallites that embed voids (Fig. 5.d). The morphology of the IOW_2 enhances the aluminothermic reaction spread, as it offers a much more surface for interaction between Al and hematite at molecular level. The particle morphology of the IOW_3 waste revealed in fig. 5 e, f is of spheroidal shape and heterogeneous in size. The open porosity has not been observed at micronic scale which can be a detrimental issue for aluminothermic recovery of this kind of waste.

The above data were used to conduct trials aimed to find out proper aluminothermic recipe for each waste type. Different termite recipes of about 100 g were tested using graphite crucibles. Every kit was ignited using a W wire that was brought to incandescence through a DC power source. The reaction products consist of iron, slag and volatile matter. Zn, Pb and As volatiles are significant in case of IOW_3 and negligible in case of IOW1 and IOW_2. The Zn, Pb and As can be recovered through selective condensation on cooled targets and/or by wet filtration as is shown in [32]. The main target of the aluminothermy is to recover the iron from waste. Therefore, the analyses are focused on the composition and microstructure of the recovered iron and less on slag characterization. The elemental composition of the iron lumps (Table 2) recovered from IOW1 and IOW2 are similar while of the one recovered from IOW3 differs as the Zn, Pb, Mg and As concentrations are significantly higher compared to those of IOW_1 and IOW ones.

Table 2.

Elemental composition of the obtained iron lumps [%]

Element	C	Si	Mn	Mg	S	P	Cr	Ni	Ti	Al	Zn	Pb	As	Fe
IOW1	0.50	0.30	1.10	0.04	0.018	0.026	0.18	0.30	0.09	0.06	0.007	0.02	0.001	97.15
IOW2	0.65	0.40	1.30	0.03	0.021	0.025	0.16	0.10	0.09	0.09	0.005	0.03	0.02	97.08
IOW3	0.07	0.54	0.10	0.21	0.032	0.045	0.12	0.21	0.07	0.12	0.020	0.08	0.005	98.38
U(95%)	0.04	0.08	0.06	0.02	0.040	0.040	0.08	0.10	0.02	0.03	0.004	0.02	0.002	0.12

The images in Fig. 6 a, c, e clearly depict the slag and the iron lump outcoming from each aluminothermic trial carried on the waste under study. The microstructures of the recovered steels differ, as can be seen in Figs. 6 b, d, f. This finding was expected because the microstructure of the recovered steel depends on the waste composition, on the thermodynamics of the aluminothermic process, which is controlled through kit content, and on the crucible size and shape [18, 16, 30].

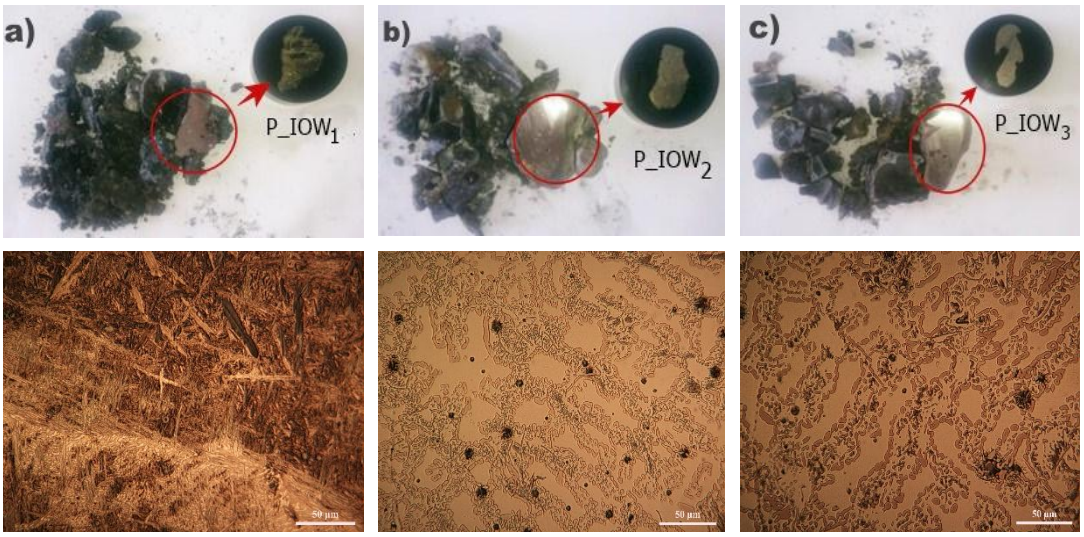


Fig 6. The slag macrostructure: a) P_ IOW_1; b) P_ IOW_2; c) P_IOW_3 and the recovered steel microstructure: b) P_ IOW_1; d) P_ IOW_2; f) P_IOW_3

The slags coming out from aluminothermic trials show up similar morphologies and quite the same phase compositions, consisting of corundum and Al-Fe compounds.

First of all, these slags can be exploited as hard ceramics for abrasive papers and, in the worst case, as fillers as they are inert and sterile in fresh stage.

4. Conclusions

The aluminothermy is an emerging technology for metallurgical solid waste recovery, but the most important, it advent as the most fitted solution for eradicating the historical dumps from Romania.

The aluminothermic technology for waste recycling critically depends on holistic waste characterization. In this regard, the paper emphasises the critical information provided by ED(P)-XRFS, XRD, SEM, SDAR-OES and metallographic methods aimed to control the effectiveness of this technology.

The paper shows up the link between the elemental composition of the waste and of the iron (steel) coming out from an aluminothermic 4R process. Also, paper points out that the microstructure of the recovered steels depends on: phase content of the waste, kit recipe, crucible shape and size.

The other contribution of the paper can be considered the introducing of the expanded uncertainty as to comply with the requirement of the standard ISO 17025:2017 and ISO 98-3:2010 when comparing the tests results.

Our findings support the need of further research on the topic of strengthening of the correlations among the waste characteristics, the technological variables and the outputs. In this regard, the method budget for

waste characterization ought to include the los-on-ignition method to gather data on organic matter, humidity and other useless substances that could be encountered in a waste dump.

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R E F E R E N C E S

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