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On the use of industrial scraps for the treatment of zinc hydrometallurgical wastes by self-propagating reactions

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Abstract

In this work the development of a technique is presented that consists of blending highly toxic solid waste from electrolytic zinc plants, i.e. paragoethite waste, with suitable amounts of aluminum, silicon, and ferric oxide, and igniting the resulting mixture so that a self-propagating front reaction rapidly travels through the mixture without requiring additional energy.

Specifically, the possibility of substituting commercial additives, needed for guaranteeing the self-propagation of the reacting mixture, with industrial scraps is demonstrated. In fact, commercial ferric oxide can be replaced by steelmaking scraps containing about 85% of iron oxides, while electronic industry by-products, characterized by Si content equal or higher than 94 wt.%, can be used instead of the corresponding commercial reactant.

Similarly to the results obtained when commercial additives were used, the main reaction product, representing 70–80 wt.% of the total mass of the original mixture and obtained when the paragoethite waste content in the starting mixture does not exceed 30 wt.%, is constituted by an alumino-silicate matrix which embodies heavy metals, such as Pb, Zn, and Cd. Leaching tests of this solid product demonstrate the fulfillment of the environmental regulations for heavy metals.

Keywords: Paragoethite waste; Industrial scraps; Self-propagating reactions

1. Introduction

It is known that zinc hydrometallurgical wastes, in the form of jarosite, goethite or paragoethite, depending on the treatment used for iron removal, are considered hazardous and toxic according to the environmental protection regulation, due to the presence of heavy metals like Pb, Cd, and Cu as well as As and Zn (cf. [1,2], and references therein).

Among the techniques proposed for the treatment of these wastes is the inertization of paragoethite wastes by self-propagating reactions, as reported recently [2,3]. It is worth noting that, these kinds of reactions, typically used for the synthesis of materials by SHS (Self-propagating high-temperature synthesis), are based on the concept that once the starting mixture is ignited by means of external thermal sources for relatively short times, highly exothermic reactions may propagate in the form of a self-sustained combustion wave leading to final products progressively without requiring additional energy [4–6].

Since paragoethite wastes typically contain up to about 50 wt.% of iron oxides, the proposed process for the inertization of these wastes was based on the use of self-propagating thermite reactions, where metallic or non metallic oxides are exothermically reduced by other metals to form more stable products [7].

After systematically investigating the effect of several reducing agents, i.e. silicon, aluminum, magnesium, and calcium, on process dynamics (self-propagating character, combustion temperature, etc.), the structure of the product, as well as the leaching behavior, it was found that [2,3] by mixing the paragoethite waste with suitable amount of commercial iron oxide, silicon, and aluminum and igniting the resulting mixture a combustion wave rapidly travels through the mixture without requiring additional energy.

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Moreover, the starting reactants completely converted into two solid products, whose main fraction consisted of an alumino-silicate phase embodying heavy metals, and a gas constituted by SO_2 [2,3].

It is worth noting that, beside the treatment of zinc hydrometallurgical wastes, self-propagating reactions were recently employed in the field of environmental protection also in other directions. In particular, interesting results have been obtained in the following areas: fixation and consolidation of high level radioactive wastes [8–10], degradation of chlorinated aromatics [11,12] and recycling of silicon sludge and aluminum dross produced by semiconductor industries and aluminum foundries, respectively [13,14]. A review paper reporting the most interesting results in this field was recently published [15].

From the economical point of view, the proposed method possesses all the advantages (relatively short synthesis time, the occurrence of self-heating to high temperatures instead of external heating, the absence of external heating elements and the simplicity of the required equipment, etc.) of SHS processes. However, the employment of commercial or, generally relatively-expensive additives, makes the proposed processes often uneconomical.

Along these lines, the aim of this work is to further investigate the self-propagating process of treatment of zinc hydrometallurgical wastes by totally or partially replacing the commercial additives previously employed in the process [2,3] with industrial scraps. Specifically, the effect of substituting the added iron oxides with a steelmaking scrap and silicon with two different types of highly Si-content industrial wastes is systematically investigated. In particular, the obtained products will be characterized from compositional and microstructural points of view as well as subjected to leaching test according to the environmental regulations currently in force in Italy.

2. Experimental section

As mentioned in Section 1, this work represents a continuation of previous studies [2,3] where the treatment of zinc hydrometallurgical wastes by self-propagating reactions was investigated. In these studies, the starting mixture consisted of a combination of commercial aluminum, silicon, and ferric oxide mixed with the waste, whose composition is reported elsewhere [3] for sake of brevity. Specifically, the amount of the reducing agents used for preparing each reacting mixture was computed according to the stoichiometry of the following thermite reactions:

$$2Fe_2O_3 + 3Si \rightarrow 3SiO_2 + 4Fe \quad (1)$$

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe \quad (2)$$

where Fe_2O_3 comes from the paragoethite waste, by assuming that its content in the waste was 44 wt.%, as well as from the commercial reactant added to the mixture in order to have the stoichiometry of Eqs. (1) and (2) satisfied.

Table 1
Composition of steelmaking scraps used for the treatment of zinc hydrometallurgical wastes by self-propagating reactions

Species	Content (wt.%)
FeO	1.42
Fe_2O_3	85.74
SiO_2	2.17
Al_2O_3	1.15
CaO	2.66
MgO	0.43
TiO_2	0.11
C	1.15
Others	5.17

Table 2
Composition of silicon scraps SiS1 used for the treatment of zinc hydrometallurgical wastes by self-propagating reactions

Species	Content (wt.%)
Si	94
Fe	1.5
C	0.8
Al_2O_3	0.3
Cu	0.3
Others	3.1

In this work, scraps from steelmaking and electronic industries were employed instead of commercial iron oxides and silicon, respectively, while maintaining the same experimental set-up and procedure adopted in the previous works [2,3]. In particular, steelmaking scraps have particles size <200 μm while the corresponding composition is reported in Table 1. It is seen that this type of scraps consists about 90 wt.% of iron oxides. Regarding the replacement of commercial silicon with industrial scraps, two types of silicon-based materials, both characterized by particles size less than 20 μm and whose compositions are shown in Tables 2 and 3, respectively, were tested. It is observed that the Si content in both scraps is higher than 94 wt.%.

A summary of the mixtures investigated by means of the technique described above is reported in Table 4. Typically, each mixture is processed in the form of cylindrical pellets (16 mm in diameter and 20 mm high) as well as loose powders placed inside a crucible. All reactions were performed under argon atmosphere.

Analogously to the previous studies [2,3], two solid products, called P_1 and P_2, and a gaseous phase are typically obtained during the propagation of the reaction. Product P_1, which represents about 70–80% of the initial mass,

Table 3
Composition of silicon scraps SiS2 used for the treatment of zinc hydrometallurgical wastes by self-propagating reactions

Species	Content (wt.%)
Si	>95
C	<5

Table 4
Summary of the mixtures investigated

Sample ID	Waste (wt.%)	Ferric oxide waste (wt.%)	Steelmaking scraps (wt.%)	Commercial Si (wt.%)	SiS1 (wt.%)	SiS2 (wt.%)	Commercial Al (wt.%)
OxS_Si_Al_a	20	8.8	59.4	9.0	–	–	11.6
OxS_Si_Al_b	25	11.0	55.2	8.7	–	–	11.1
OxS_Si_Al_c	30	13.2	50.8	8.4	–	–	10.8
OxS_Si_Al_d	35.7	15.7	45.8	8.1	–	–	10.4
OxS_Si_Al_e	44.6	19.6	38.0	7.6	–	–	9.7
OxS_Si_Al_f	53.6	23.6	30.2	7.1	–	–	9.1
OxS_Si_Al_g	62.5	27.5	22.5	6.6	–	–	8.4
OxS_SiS1_Al_a	20	8.8	59.4	–	9.0	–	11.6
OxS_SiS1_Al_b	25	11.0	55.2	–	8.7	–	11.1
OxS_SiS1_Al_c	30	13.2	50.8	–	8.4	–	10.8
OxS_SiS1_Al_d	35.7	15.7	45.8	–	8.1	–	10.4
OxS_SiS1_Al_e	44.6	19.6	38.0	–	7.6	–	9.7
OxS_SiS1_Al_f	53.6	23.6	30.2	–	7.1	–	9.1
OxS_SiS1_Al_g	62.5	27.5	22.5	–	6.6	–	8.4
OxS_SiS2_Al_a	20	8.8	59.4	–	–	9.0	11.6
OxS_SiS2_Al_b	25	11.0	55.2	–	–	8.7	11.1
OxS_SiS2_Al_c	30	13.2	50.8	–	–	8.4	10.8
OxS_SiS2_Al_d	35.7	15.7	45.8	–	–	8.1	10.4
OxS_SiS2_Al_e	44.6	19.6	38.0	–	–	7.6	9.7
OxS_SiS2_Al_f	53.6	23.6	30.2	–	–	7.1	9.1
OxS_SiS2_Al_g	62.5	27.5	22.5	–	–	6.6	8.4

remains where the unreacted pellet was placed inside the reactor, while product P_2 gets distributed in powder form on the walls of the reaction chamber as a consequence of a probable expulsion occurring during the course of the reaction.

The temperature during reaction evolution was measured using thermocouples (W–Re, 127 μm diameter, Omega Engineering Inc.) embedded in the pellet.

The solid products were characterized by X-ray diffraction (XRD) using the Ni-filtered Cu Kα radiation on a Philips PW-1830 diffractometer. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) microanalysis (HITACHI S 4000 Field emission equipped with a KEVEX SIGMA 32 probe at a resolution of 142 eV) were also used to characterize the microstructure of the final products.

The leaching behavior of the products was evaluated according to the Italian Environmental Regulation (IER), i.e. D.L. 5 February 1997, n. 22. The test consists of contacting the solid product with distilled water in 1:5 weight ratio, with the water replaced eight times at fixed periods. A proper amount of 1 M nitric acid solution is then added to each eluate sample until a pH equal to 2 is reached. The resulting solutions are then analyzed separately by inductively coupled plasma atomic absorption (ICP-AA) in order to determine the concentration of the monitored toxic species. The concentration, to be compared with the maximum allowable value according to the Italian environmental regulations, results from the sum of the concentration values related to the eight solutions obtained following the procedure reported above.

3. Results and discussion

3.1. Use of steelmaking scraps

Reacting mixtures where commercial ferric oxide was replaced with equal amount of the steelmaking scrap were first investigated. The occurrence of self-propagating reaction and maximum temperature recorded during the reaction wave, is reported in Table 5. It was found that, if the content of zinc wastes into the starting mixture was equal or lower than 53.6 wt.%, the mixture is characterized by an SHS behavior. In addition, the Table shows that the temperature values decrease with increasing waste content as the exothermicity of the starting mixture becomes lower. In particular, waste amounts equal or larger than 62.5 wt.% result in mixtures which are not able to self-propagate.

The X-ray diffraction patterns of products P_1 obtained for the different mixtures reported in Table 5 are shown in

Table 5
Reaction behavior of the reacting mixtures investigated when steelmaking scraps are used instead of commercial ferric oxide

Sample ID	Waste (wt.%)	Self-propagation	Maximum temperature (K)
OxS_Si_Al_a	20.0	Yes	–
OxS_Si_Al_b	25.0	Yes	–
OxS_Si_Al_c	30.0	Yes	2005
OxS_Si_Al_d	35.7	Yes	1953
OxS_Si_Al_e	44.6	Yes	1914
OxS_Si_Al_f	53.6	Yes	1897
OxS_Si_Al_g	62.5	No	–

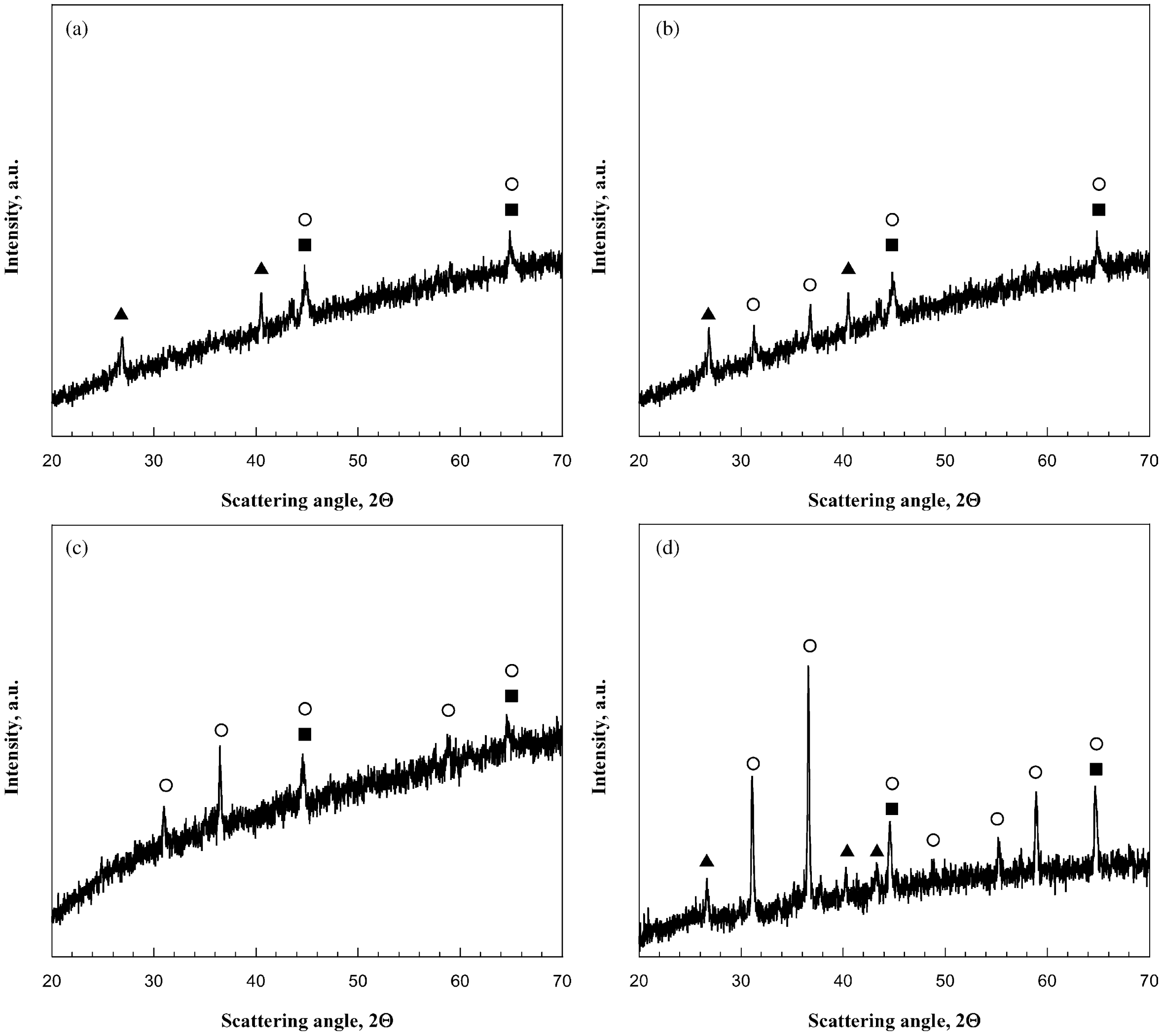

Fig. 1. XRD spectra of product P_1 obtained when reacting mixtures where the commercial ferric oxide is replaced by steelmaking scraps: (a) OxS_Si_Al_c, (b) OxS_Si_Al_d, (c) OxS_Si_Al_e, and (d) OxS_Si_Al_f samples; (○) $FeAl_2O_4$, (■) Fe, (▲) SiO_2.

Fig. 1. It is seen that the only crystalline phases detected are hercinite ($FeAl_2O_4$), SiO_2, and Fe.

Analogously to the results reported in previous works [2,3] where commercial ferric oxide was employed, XRD analyses of solid product P_2 indicate the presence of lead and zinc, iron and zinc sulfides, zinc arsenide as well as some traces of reactants, especially Al and Si, which are expelled during the reaction evolution. Due to its composition, product P_2 can be therefore recycled in the sphalerite roasting unit of the zinc production plant, as already proposed in the cited studies [2,3].

Products P_1 were further characterized by SEM and WDS microanalysis, in order to identify their microstructure as well as the presence of other species which cannot be revealed by XRD analysis because of their non crystalline nature or their relative low content. As an example, an SEM back-scattered electron micrograph obtained when reacting the sample OxS_Si_Al_c is reported in Fig. 2. The results

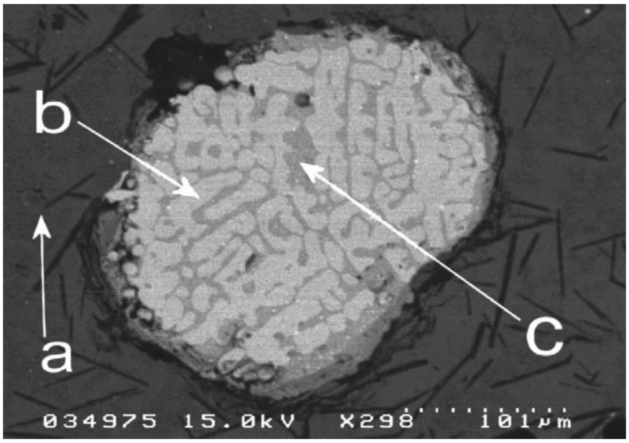

Fig. 2. SEM back-scattered views of the microstructure of the product P_1 obtained when reacting mixtures where the commercial ferric oxide is replaced by steelmaking scraps (sample OxS_Si_Al_c).

Table 6
Analysis of eluate from leaching tests on the fraction P_1 for products obtained when steelmaking scraps are used instead of commercial ferric oxide

Sample ID	Cu (mg/l)	Zn (mg/l)	Cd (mg/l)	Pb (mg/l)
OxS_Si_Al_c	0.026	0.96	<0.001	0.028
OxS_Si_Al_e	0.08	1.17	<0.001	0.054
OxS_Si_Al_f	0.13	2.28	0.007	0.076
Maximum allowable concentration	0.05	3	0.005	0.05

are similar to those obtained using commercial additives [2,3]. In fact, the product is constituted by small globules dispersed into a dark region (a). The latter one consists of alumino-silicates of iron while two different zones can be easily identified inside the globules. The lighter region, indicated by (b) in Fig. 2, is very rich in iron, while the darker one (c) still contains iron with lead particles finely dispersed.

Products P_1 are then subjected to leaching tests according with the Italian Environmental Regulation. The obtained results are shown in Table 6 for the case of 30, 44, and 53.6 wt.% of waste in the starting mixture. It is seen that the only sample which passed the test is OxS_Si_Al_c, i.e. the one corresponding to a waste percentage equal to 30 wt.%, while higher lead concentration values were found in the leachate for the other mixtures examined.

3.2. *Use of steelmaking and silicon-rich scraps*

As shown in Table 4, the reacting mixtures examined in this paragraph differ from those considered in the previous one because commercial silicon has been also replaced by scraps coming from industries which produce electronic components. Specifically, two different silicon rich wastes, hereto after named SiS1 and SiS2, respectively, were tested. The self-propagating behavior of the obtained mixtures along with the maximum combustion temperature recorded during wave propagation are reported in Tables 7 and 8, for the case of SiS1 and SiS2, respectively. No significant differences were observed if compared to the case previously discussed. In particular, the same boundary, i.e. waste content equal to 62.5 wt.%, below which it is possible to guarantee the self-propagating character to the reacting process, was found. Moreover, similar values and identical temperature trends were found as the amount of the zinc waste in the reacting mixture was augmented.

Table 7
Reaction behavior of the reacting mixtures investigated when scraps from steelmaking and silicon (SiS1) are used instead of commercial ferric oxide and silicon, respectively

Sample ID	Waste (wt.%)	Self-propagation	Maximum temperature (K)
OxS_SiS1_Al_a	20.0	Yes	2312
OxS_SiS1_Al_b	25.0	Yes	2043
OxS_SiS1_Al_c	30.0	Yes	1998
OxS_SiS1_Al_d	35.7	Yes	1989
OxS_SiS1_Al_e	44.6	Yes	1782
OxS_SiS1_Al_f	53.6	Yes	1644
OxS_SiS1_Al_g	62.5	No	–

Table 8
Reaction behavior of the reacting mixtures investigated when scraps from steelmaking and silicon (SiS2) are used instead of commercial ferric oxide and silicon, respectively

Sample ID	Waste (wt.%)	Self-propagation	Maximum temperature (K)
OxS_SiS2_Al_a	20.0	Yes	2319
OxS_SiS2_Al_b	25.0	Yes	2083
OxS_SiS2_Al_c	30.0	Yes	1980
OxS_SiS2_Al_d	35.7	Yes	1882
OxS_SiS2_Al_e	44.6	Yes	1720
OxS_SiS2_Al_f	53.6	Yes	1637
OxS_SiS2_Al_g	62.5	No	–

The results of X-ray diffraction analyses of products P_1 obtained for the different mixtures reported in Tables 7 and 8 are shown in Figs. 3 and 4, when SiS1 and SiS2 are employed, respectively. Here, slight differences were found as compared to the results reported in the previous paragraph, as well as for the case of commercial additives [2,3]. In fact, the hercinite reflections are generally much more evident for all mixtures investigated, as shown in the corresponding X-ray patterns. A similar situation was obtained using commercial silicon only for the case of relatively higher paragoethite waste content in the mixture, i.e. 53.6 wt.%. Since the maximum temperatures are approximately the same, the relatively intensive hercynite crystallization observed in this case may be related to slower cooling rates occurring when the commercial reactant is replaced with silicon scraps. Although the presence of impurities in the latter one may play a role in this direction, at this stage no reasonable justification were found for this. However, as it will be shown later, this fact does not produce significant differences in the leaching behavior.

On the other hand, similar results were obtained regarding the composition of the minor solid product P_2, being lead, zinc, iron and zinc sulfides, zinc arsenide, Al, and Si, the species identified. Therefore, also in this case product P_2 can be recycled in the roasting unit of the zinc production plant.

Two examples of the SEM investigation of product P_1 are reported in Figs. 5 and 6 for the cases of OxS_SiS1_Al_c and OxS_SiS2_Al_c systems, respectively. In particular, a back scattered micrographs together with the corresponding Fe, Cu, and Pb maps are reported in both figures for each sample. The results are similar to those previously discussed. In fact, both products are constituted by small globules dispersed into a dark matrix. The latter one consists of

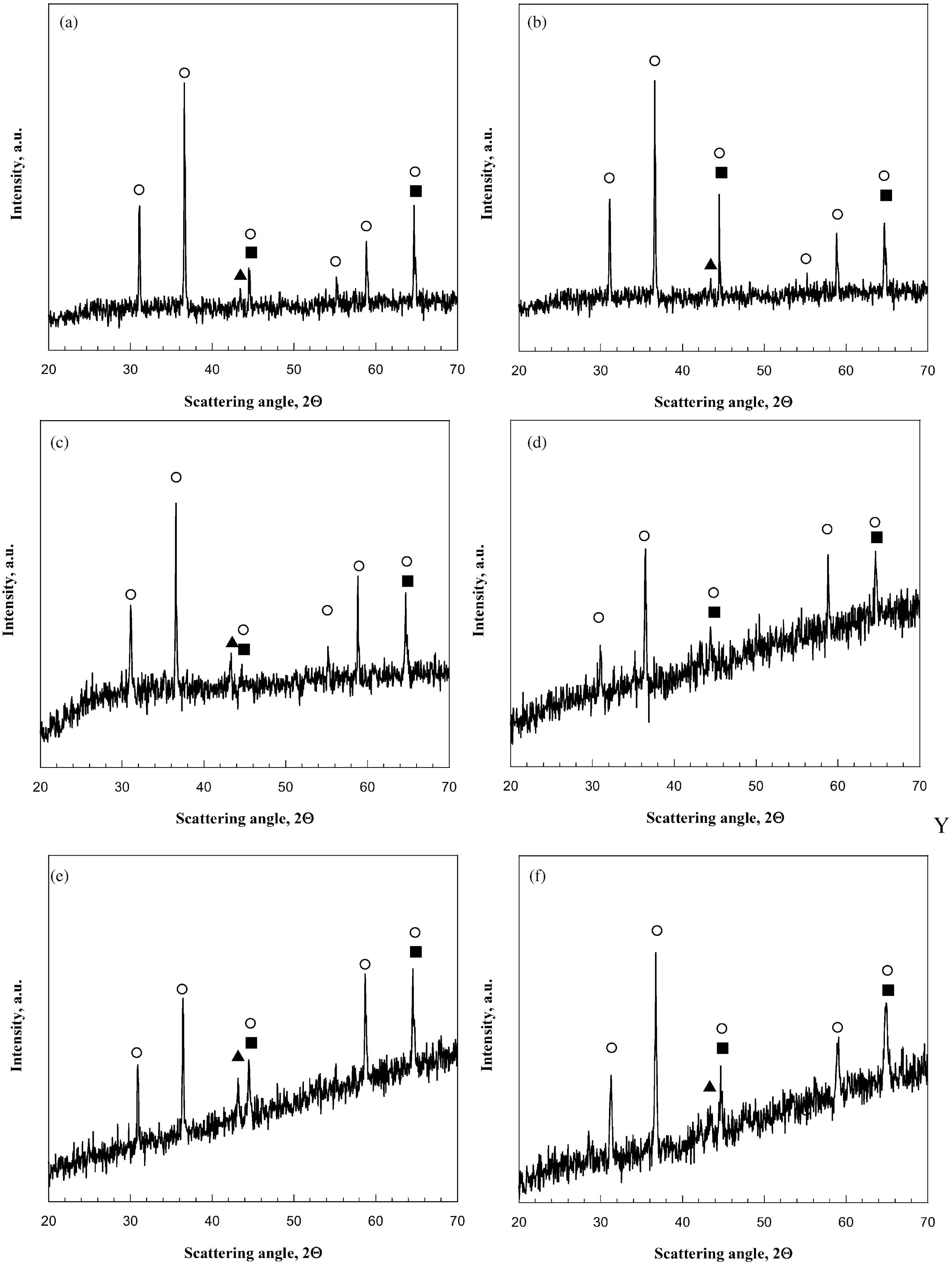

Fig. 3. XRD spectra of product P_1 obtained when reacting mixtures where both commercial ferric oxide and silicon are replaced by steelmaking scraps and silicon scraps (SiS1), respectively: (a) OxS_SiS1_Al_a, (b) OxS_SiS1_Al_b, (c) OxS_SiS1_Al_c, (d) OxS_SiS1_Al_d, (e) OxS_SiS1_Al_e, and (f) OxS_SiS1_Al_f samples; (○) $FeAl_2O_4$, (■) Fe, (▲) SiO_2.

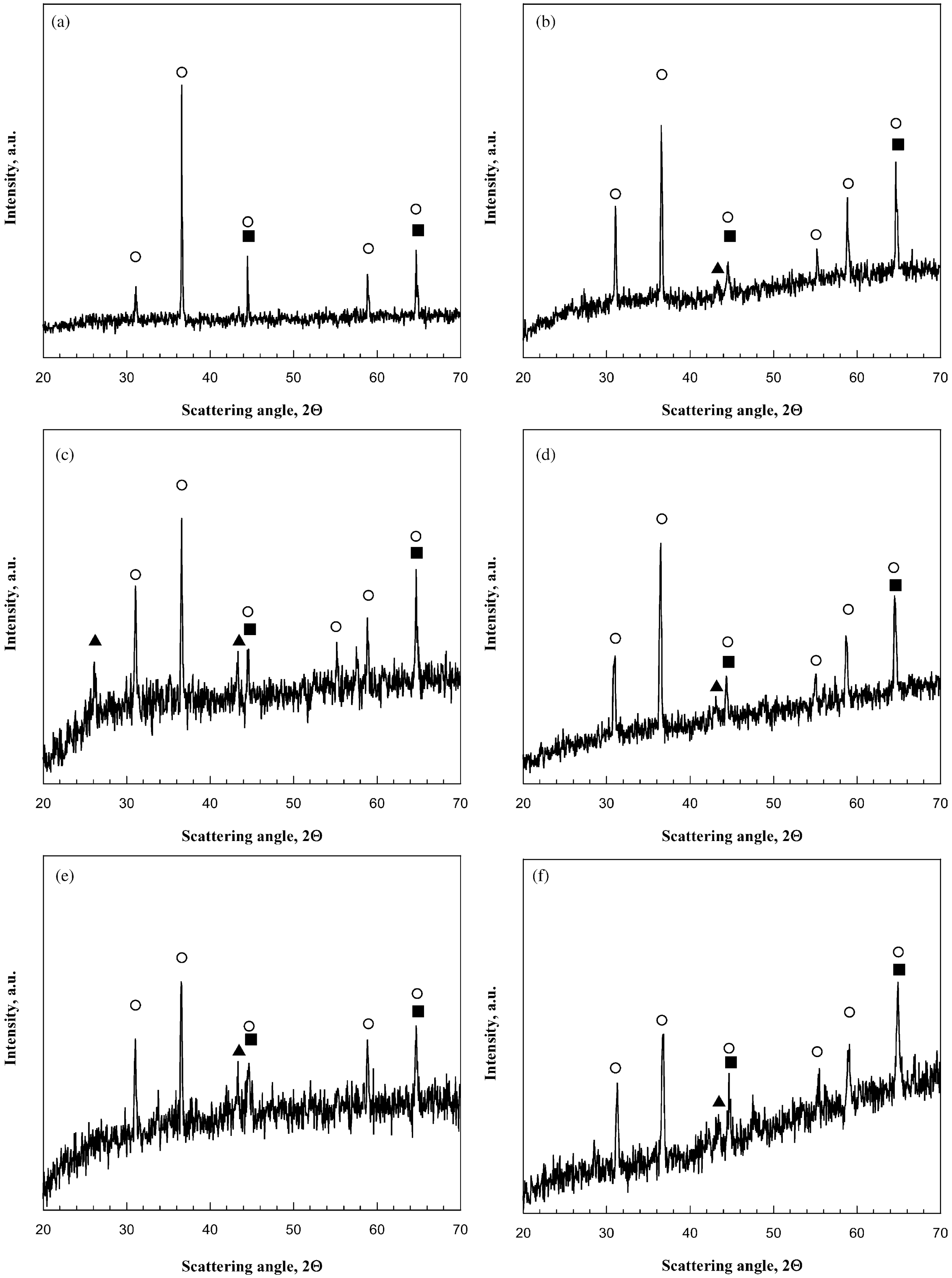

Fig. 4. XRD spectra of product P_1 obtained when reacting mixtures where both commercial ferric oxide and silicon are replaced by steelmaking scraps and silicon scraps (SiS2), respectively: (a) OxS_SiS2_Al_a, (b) OxS_SiS2_Al_b, (c) OxS_SiS2_Al_c, (d) OxS_SiS2_Al_d, (e) OxS_SiS2_Al_e, and (f) OxS_SiS2_Al_f samples; (○) $FeAl_2O_4$, (■) Fe, (▲) SiO_2.

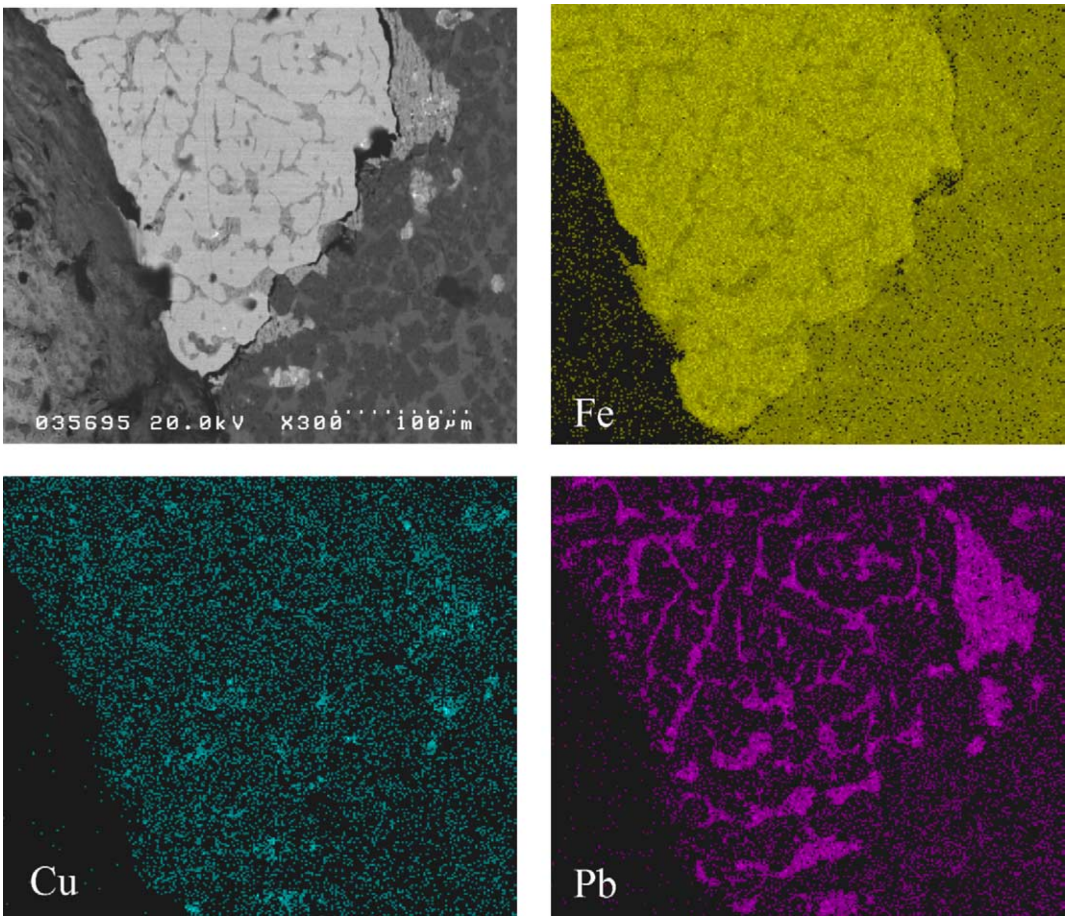

Fig. 5. SEM back-scattered views of the microstructures of the product P_1, along with the corresponding Fe, Cu, and Pb maps, obtained when reacting mixtures where the commercial ferric oxide and silicon are replaced by steelmaking scraps and silicon scraps (SiS1), respectively (sample OxS_SiS1_Al_c).

alumino-silicates, where crystals of hercinite are well evident, especially for the case reported in Fig. 5. This result is consistent with what we already observed via X-ray analysis (Figs. 3 and 4). On the other hand, the lighter globules are similar to those previously seen. In addition, the maps revealed that iron and, more important, lead, are significantly concentrated inside them. This is an important aspect since it means that this hazardous heavy metal, initially present in the waste at relatively high content, is mainly confined in relatively small regions surrounded by a silicate matrix.

Table 9
Analysis of eluate from leaching tests on the fraction P_1 for products obtained when the commercial ferric oxide and silicon are replaced by steelmaking scraps and silicon scraps (SiS1), respectively

Sample ID	Cu (mg/l)	Zn (mg/l)	Cd (mg/l)	Pb (mg/l)
OxS_Si1_Al_c	0.03	2.48	<0.001	0.04
OxS_Si1_Al_e	0.046	3.27	0.007	0.047
OxS_Si1_Al_f	0.08	3.47	0.012	0.073
Maximum allowable concentration	0.05	3	0.005	0.05

Analogously to the cases previously investigated and discussed, products P_1 obtained starting from mixtures containing silicon wastes were subjected to leaching tests according to the Environmental Regulation currently in force in Italy. The obtained results are shown in Tables 9 and 10, for the case SiS1 and SiS2 scraps types, respectively. Specifically, these results refers to 30, 44, and 53.6 wt.% of zinc waste in the initial samples.

Again, for both situations, it is seen that the only samples which passed the test where those corresponding to 30 wt.% of paragoethite waste in the reacting mixture.

Table 10
Analysis of eluate from leaching tests on the fraction P_1 for products obtained when the commercial ferric oxide and silicon are replaced by steelmaking scraps and silicon scraps (SiS2), respectively

Sample ID	Cu (mg/l)	Zn (mg/l)	Cd (mg/l)	Pb (mg/l)
OxS_Si2_Al_c	0.026	1.95	<0.001	0.023
OxS_Si2_Al_e	0.036	2.89	0.009	0.057
OxS_Si2_Al_f	0.07	3.65	0.011	0.062
Maximum allowable concentration	0.05	3	0.005	0.05

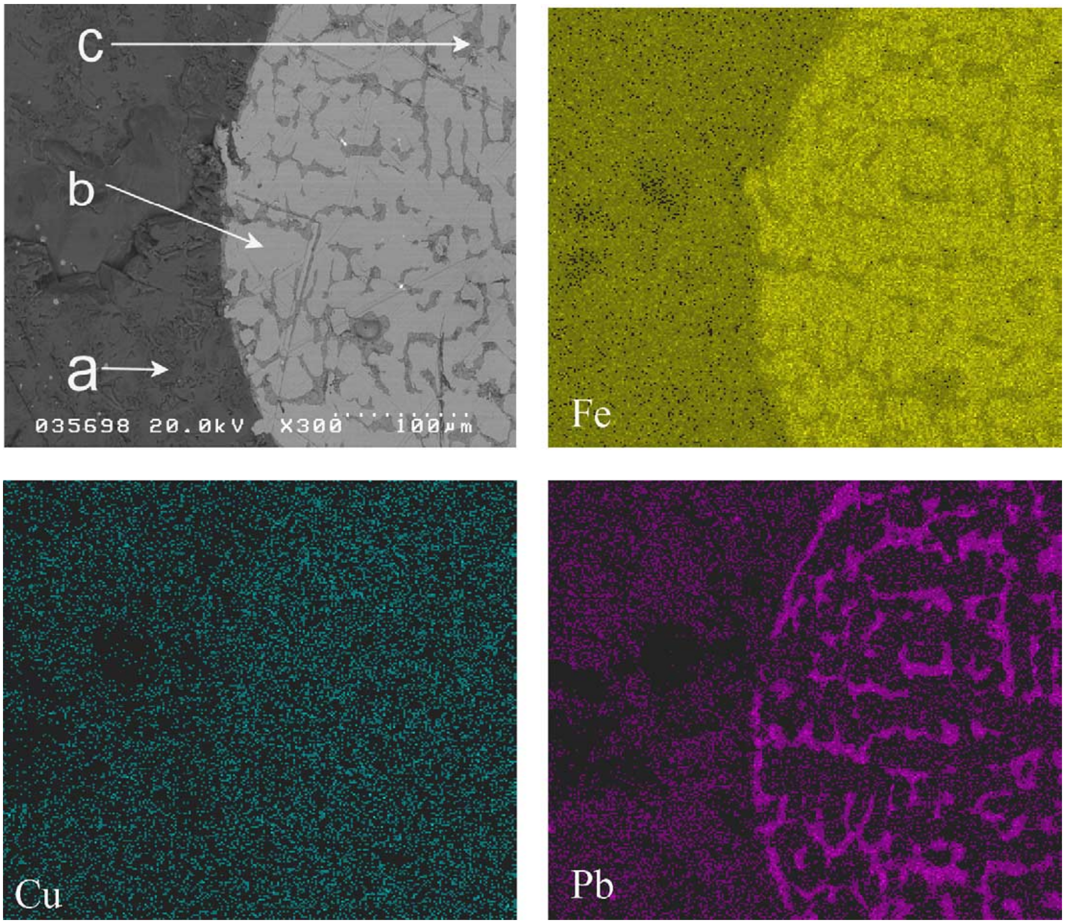

Fig. 6. SEM back-scattered views of the microstructures of the product P_1, along with the corresponding Fe, Cu, and Pb maps, obtained when reacting mixtures where the commercial ferric oxide and silicon are replaced by steelmaking scraps and silicon scraps (SiS2), respectively (sample OxS_SiS2_Al_c).

4. Concluding remarks

As mentioned in Section 1, this work represents a natural extension of previous investigations [2,3] regarding a novel technique for the treatment of paragoethite wastes by self-propagating reactions. Specifically, the main objective of this work was to totally or partially substitute the commercial additives, i.e. silicon, ferric oxide, and aluminum, needed to make the process self-sustaining, with other alternative low cost materials. Of course, the reduction of the cost of the process should always be complemented by similar results in terms of product inertization.

The results shown above demonstrated that, starting from a mixture containing 30 wt.% of paragoethite wastes, the substitution of commercial silicon and ferric oxides with Si rich wastes (Si content higher than 94 wt.%) and Fe_2O_3 rich steelmaking (containing about 85% of iron oxides) scraps provides reaction products analogous to those corresponding to commercial additives, where the toxic species are incorporated inside a silicate matrix.

In addition, leaching test results confirm that the formation of the alumino-silicate phase which encapsulates the toxic species originally present in the waste leads to a highly water resistant material. This represents an important result from the environmental point of view in the framework of preventing groundwater and surface water contamination.

On the basis of the results obtained in this work, the starting mixture leading to the product which passes the leaching test consists of about 90 wt.% of wastes [16]. It is worth noting that selected experiments were performed using air instead of argon. The obtained results were analogous, as expected from previous investigation where commercial reactants, except for paragoethite, were used [2]. Further, additional cost reduction may be achieved through the replacement of commercial aluminum with analogous low-cost materials. Although aluminum-based scraps are difficult to find or convert to powder form, as required by the proposed process, work is in progress along this direction.

As the economic aspects of this process are more specifically taken into account, it is worth mentioning that SHS is an efficient process because of its relatively short synthesis time, the occurrence of self-heating up to high temperatures instead of external heating, the absence of external heating elements and the simplicity of equipments required

[17–19]. These intrinsic characteristics of SHS processes hold also true when dealing with self-propagating reactions for environmental protection. A detailed investigation of economic efficiency of SHS processes is typically performed by comparing physical parameters of SHS products with existing analogues. This procedure is in general extremely hard to carry out because of the lack of accessible 'know-how' information [19]. For the case of the recycling and treating of wastes by self-propagating reactions such an investigation is even more difficult, due to the lack of existing industrial applications. However, the procedure for analyzing the treatment costs is constituted first by the description of the process steps followed by the definition of the unit costs for each category, i.e. raw materials, fixed costs, utilities, disposable materials, labor, that form the basis of the cost analysis [17]. In particular, it was found that fixed costs are generally lower for SHS-based process as compared to conventional ones. On the other hand, while raw materials costs are often higher when synthesizing materials by SHS, this cost category may be drastically reduced for the case of self-propagating reactions for environmental protection, because recycled materials may be used as reactants, as considered in this work.

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