

Microstructural characterization of a goethite waste from zinc hydrometallurgical process

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Abstract

The different hydrometallurgical processes for the metallic zinc recovery produce a high quantity of wastes in the form of muds that at the moment are stored within the production plants in large clamps without until now may have been found an effective way for their recycling. A possible solution for these wastes would be the utilization of the vitrification and glass ceramic materials technology. Because of this, the characterization of a goethite waste has been accomplished. The results of the granulometric analysis, chemical, mineralogic, microstructural characterization and thermal analysis demonstrate that the goethite waste, mixed with other raw materials can be used in the formulation and production of glasses and glass ceramics.

Keywords: Goethite; Industrial waste; Red mud; Hydrometallurgy; Glass ceramics

1. Introduction

The chemical processes for the metallic zinc manufacture can be of several types, that can be summarized basically as: (a) goethite process (FeOOH) and (b) jarosite process ($\text{MFe}_3(\text{SO}_4)_2(\text{OH})_6$). In both a great quantity of wastes are produced, giving rise to an approximate waste production in the European Union about 600.000 ton/year.

Nowadays, the great volume of wastes produced from the zinc hydrometallurgic industry is stored in different types of closed containers or in sealed reservoirs near of the production plants. Governmental and environmental actions are being directed in

some countries of the EU in order to avoid pollution problems, besides the problems of great space or soil occupation (already expensive and scarce) in practically all areas which have installed industries that generate these wastes. For this reason, in order to recover valuable elements, the companies are working in future treatment processes of the waste to produce an useful material for the steel manufacture or at least, to transform them into other forms less prejudicial for the environment. As a possible solution to the storage and inertization of these wastes the "Jarochaux" process has been proposed. This implies the mixture of the mud with a concentrate of lime [1]. The inertization, storage and even recycling of muds is a common topic to other hydrometallurgic processes and it has been proposed various solutions such as the use of these muds as construction material [2], catalysts and pigments [3] or refractories [4].

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On the other hand, a lot of scientific and technological research has been carried out in glasses and glass ceramics production with different applications, from domestic uses to advanced applications, whose technology would be used to find a solution to the economic and ecological problem mentioned above. There is no previous work for recycling these wastes by using the traditional technology in the glassy and ceramic materials production [5,6].

The aim of this work is to accomplish the complete characterization of a goethite waste originated from the zinc hydrometallurgy that afterwards is going to be used as raw materials in the glassy and glass ceramic materials manufacture.

2. Experimental

The goethite waste originated from the factory of Nuova Samín (Sardinia, Italy) was supplied by the Institute of Minerals Treatment of Rome (CNR) in the form of red color mud. The waste has been homogenized through agitation, being determined its density, humidity content and size of particle. Afterwards, the mud was filtered and split into two samples:

The first sample was dried to 70°C during 12 h in order to eliminate part from the humidity content without proceed to more alterations of these raw materials. The obtained sample was submitted to chemical and mineralogic analysis, determination of density, differential thermal analysis, microstructural observation and determination of the contraction curve.

The second sample was separated by means of a cyclone in six particle sizes that were submitted to chemical and mineralogic analysis.

In every case, the qualitative analysis has been carried out through an X-ray fluorescence (XRF) Philips PW 1406 equipment. The quantitative analysis has been accomplished by inductive coupling spectroscopy of plasma emission (ICP) using a Jobin-Yvon JV-38 VHR equipment, as well as atomic absorption spectroscopy in a Perkin-Elmer 305 equipment. The granulometric analysis has been carried out with a Sympatec Helos 12LA equipment. The test of X-ray diffraction has been accomplished with an XRD diffractometer, Siemens Diffraktometer

D5000, with K_{α} Cu radiation, working to 30 mA and 50 kV in samples grounded until their step by sieve of 37 μm . For the microstructural observations an electronic microscope (digitized Zeiss DSM-950) has been used under acceleration tension of 20 kV and with an microanalysis system by dispersion of X-ray energies (EDX), Tracor Northem ZX-II. The heating microscopy tests have been accomplished with a high temperature microscope Leitz-II-A-P with pulverized sample and pressed in the form of cylinders of 2 mm diameter and 3 mm height over alumina support. The heating rate was 10°C/min. The DTA test as well as those of TG have been carried out with a Mettler TA equipment with platinum crucibles, using alumina calcined as reference standard, in air atmosphere with flow of 12 l/h and to heating rate of 10°C/min.

3. Results and discussion

Once homogenized, the mud sample of the original goethite has a humidity content between 44 and 47% and a mean density of 3.77 g/cm³.

3.1. Granulometric analysis

The accumulated distribution function and the distribution density results have indicated that the mean size of particle is relatively fine; 80% of the sample showing a size lower than 23 μm . The size curve distribution presents three differentiated peaks that indicate the possible existence of three populations. For the interpretation of this granulometric analysis, the data have been linearized according to the equation of Rosin-Rammler [7]:

$$W(\%) = 100 e^{-(X_0/X)^b},$$

where b is proportional to the dispersion of the particles size in a given size range. In Fig. 1 are given the results of such linearization. The three lines illustrate the existence of three populations of particle size, probably related to the number of phases that are formed during the precipitation of goethite.

3.2. Chemical composition

The chemical analysis of goethite, qualitative as well as quantitative, has been performed in the origi-

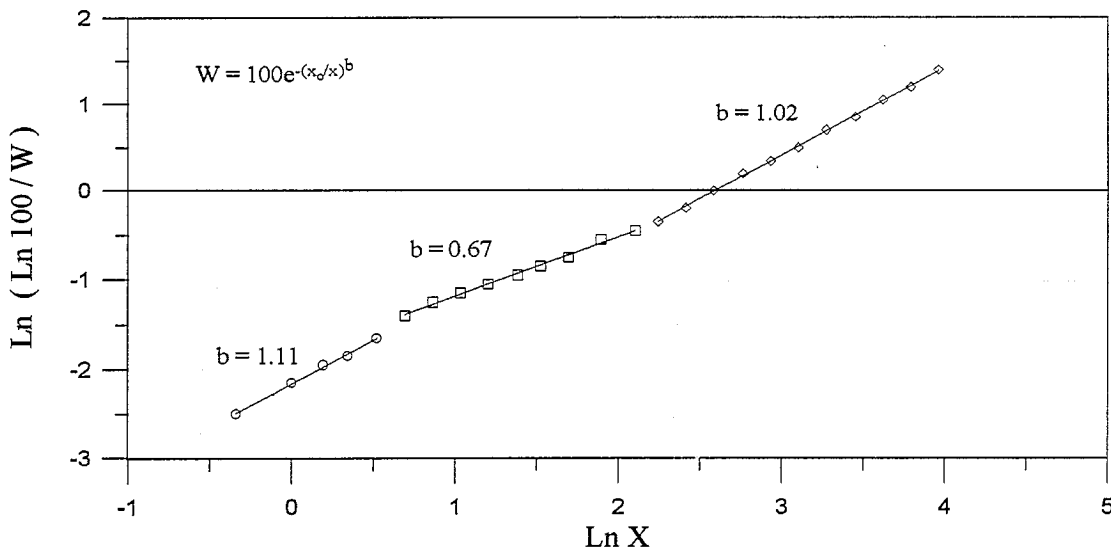


Fig. 1. Particle size distribution of goethite linearized by the Rosin–Rammler equation.

nal sample and also in the six samples of the resulting particle size of the separation carried out in cyclone. There are no important differences between them. The qualitative analysis has detected the following elements: Fe, Zn, Pb, Si, Ca, Cu, K, Ti, Sn and Al. With respect to quantitative chemical analysis, in all the cases the sample contains Cd, Na, As and Co as minor elements. Table 1 shows the chemical analysis of the goethite waste.

3.3. Mineralogy

Fig. 2 shows the corresponding X-ray diffractograms of the goethite sample and the obtained fractions from the separation of particles. The presence of goethite (α -FeO(OH)), maghemite (γ -Fe₂O₃) and magnetite (Fe₃O₄) has been identified. Besides these phases, also sulphates can be present in small different proportions such as Fe₂(SO₄)₃ · H₂O, ZnSO₄ · H₂O and CaO.2H₂O, since small peaks are detected that they could belong to these compounds. It is observed that the number of peaks reduces upon making the particle size smaller. This effect can be due to a great amorphization in the fine fractions more than to a disappearance of the corresponding phases. The distances between the peaks in the fine fractions are the same as that in the total sample, indicating no enrichment in a mineral phase determined from a particle size interval.

3.4. Microstructure

With the purpose of examining directly the microstructure of the goethite waste, it has been accom-

Table 1
Chemical analysis of goethite red mud

Oxide	Weight ^a (%)
Fe ₂ O ₃	51.28 ± 1.49
ZnO	13.29 ± 0.61
PbO	6.27 ± 0.04
SiO ₂	2.91 ± 0.15
CaO	0.98 ± 0.003
Al ₂ O ₃	0.70 ± 0.01
CuO	0.46 ± 0.0001
As ₂ O ₃	0.29
NiO	0.29
CdO	0.08 ± 0.0001
Na ₂ O	0.06 ± 0.0001
TiO ₂	0.05 ± 0.01
SnO ₂	0.05 ± 0.01
K ₂ O	0.05 ± 0.0001
CO ₂	0.78
SO ₂	10.34
LOI ^b	12.61 ± 0.27
Co	30 ppm
Te	3 ppm
Total	99.37

^a Average value for five tests; exception made for iron determination (four tests)

^b Temperature: 860°C.

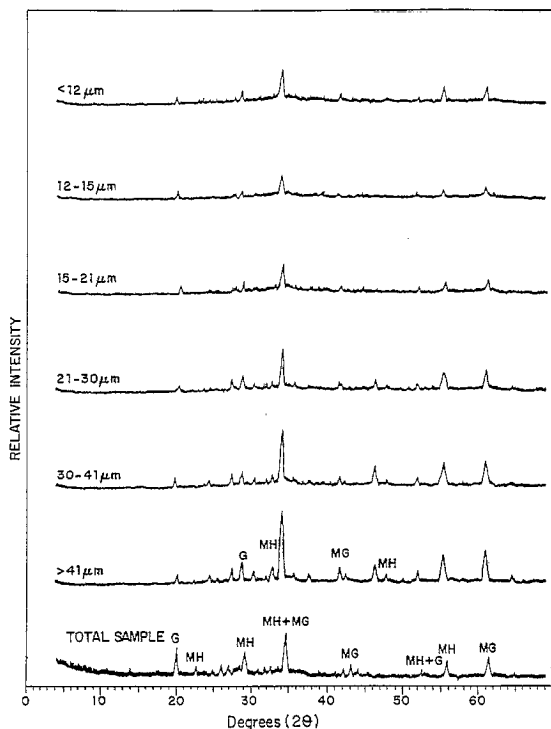


Fig. 2. XRD diffractograms for the goethite sample and for each different size fraction (MG = magnetite; G = goethite; MH = maghemite).

plished by scanning electron microscopy (SEM) on a mud sample desiccated at 70°C for 12 h. Samples have been pressed as cakes in order to facilitate the

conduction between the grains and to avoid the charge accumulation of electrons that would impede the observation. Fig. 3 shows the texture of this material. It is appreciated that it is constituted of very fine size particles (smaller than 0.1 μm) which are agglomerated for the most part to grains close to 1 μm, having the grains as well as the smaller size particles in irregular form.

3.5. Infrared spectroscopy

Fig. 4 shows the infrared spectrum (IR) of a sample of goethite in a KBr matrix. In the 2000–4000 cm^{-1} region, a wide absorption band appears which can be assigned to the stretching modes of water molecules adsorbed on the goethite surface [8] or to envelope of H-bonded surface OH groups, whereas the characteristic band at 1630 cm^{-1} is due to the H_2O bending mode.

According to Ref. [9,10], the bands which appear at 1130 and 980 cm^{-1} are attributed to ν_1 and ν_3 vibrations of surface adsorbed SO_4^{2-} ions. Otherwise, Goñi et al. [10] have detected shoulders at 1040 and 1200 cm^{-1} which they attributed also to SO_4^{2-} , which could correspond to other (ν_2 and ν_4) vibrations. However, it is reported in Ref. [10] that these bands could also be deformation vibrations of the surface OH groups of amorphous iron hydroxides which have true hydroxide structure and not hydrated iron oxide. On the other hand, according to

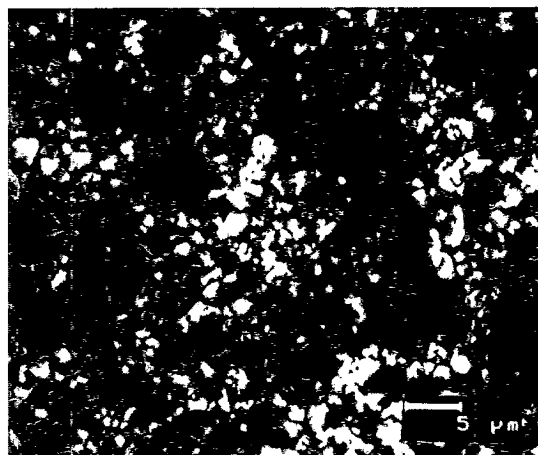
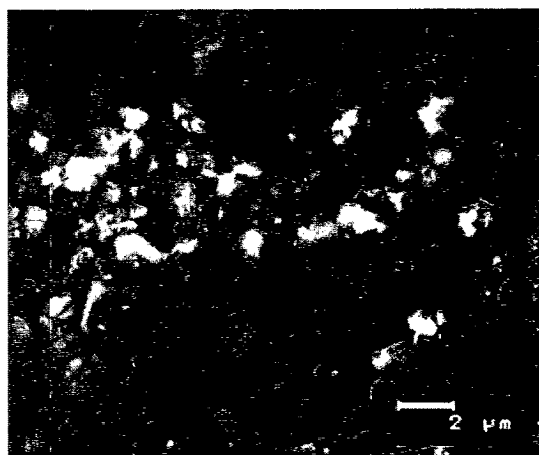


Fig. 3. SEM micrograph of the goethite dried at 70°C/12 h (the specimen was prepared as a cylindrical cake).

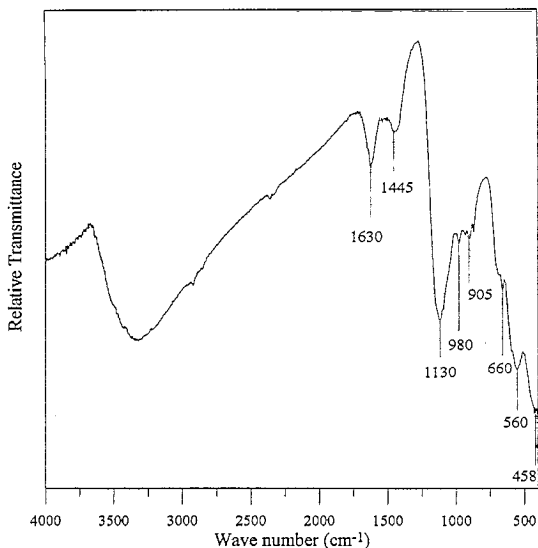


Fig. 4. IR spectrum of the goethite waste in a KBr matrix.

the same authors, the 905 cm^{-1} band actually is the well-known 880 cm^{-1} goethite band, which here is shifted to higher wave numbers due to the high water contents of the goethite red mud considered here. Moreover, though the 660 cm^{-1} and other (458 and

560 cm^{-1}) bands are attributed to goethite [11], Mendelovici et al. [12] assign this band to an intermediate compound named protohematite which usually is formed when goethite is heated.

3.6. Thermal analysis

Fig. 5 shows the DTA/TG curve for the goethite sample after desiccation at $70^\circ\text{C}/12\text{ h}$. As can be observed in the TG curve, in the $25\text{--}400^\circ\text{C}$ range there is a continuous loss of weight due to the volatilization of water. The inflection point found between 150°C and 170°C by different authors in the study of synthetic goethite has not been observed. This inflection reflects the difference between the adsorbed water and the structural water. Therefore, we can consider that the goethite sample investigated here does not show an adsorption layer. This first loss corresponds to the 13% weight, which is greater than the loss of the theoretical weight (10.1%) according to Paterson et al. [13]. This difference between the theoretical and experimental values reflects probably: (a) an excess in the OH content due to the surface protonation of the oxides and (b) coordination of atmospheric OH with the Fe^{3+} ions located in the edges of the crystals.

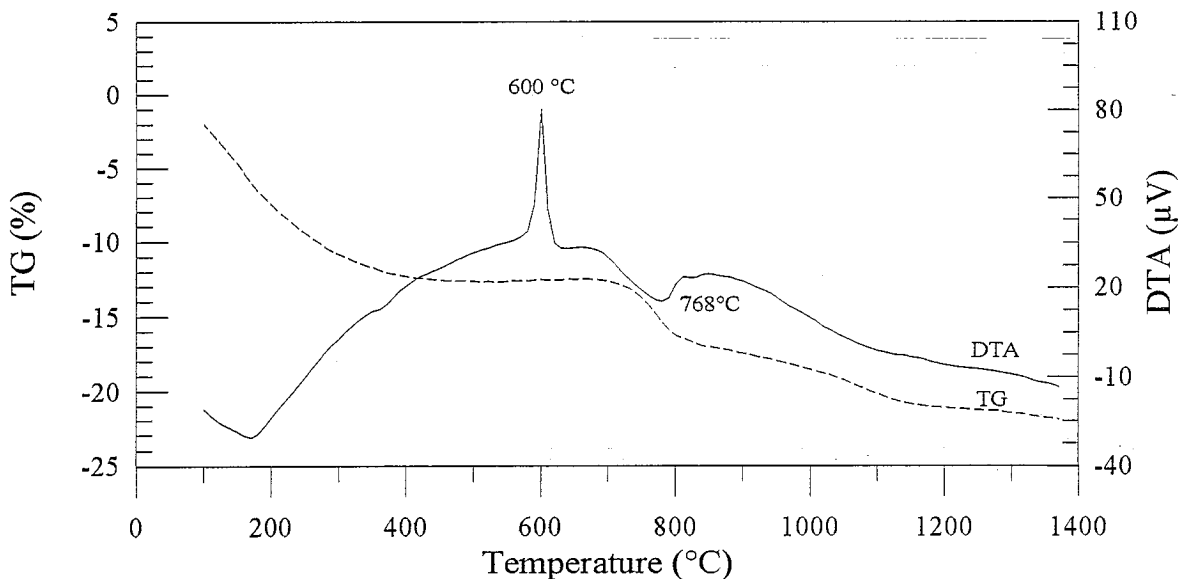


Fig. 5. DTA/TG thermogram obtained from a goethite red mud dried at $70^\circ\text{C}/12\text{ h}$.

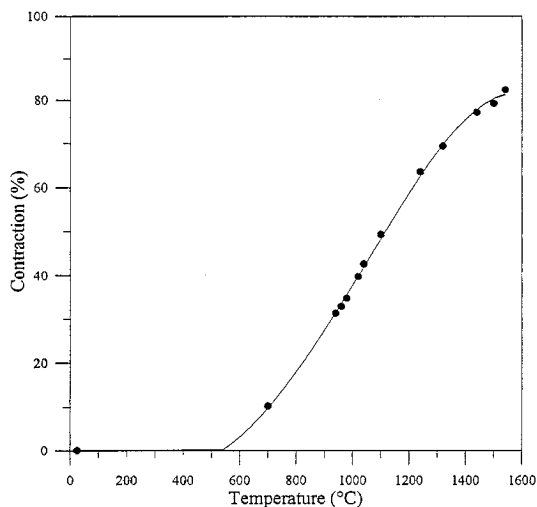
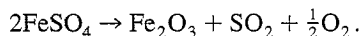


Fig. 6. Contraction curve (heating microscopy) from a red mud goethite sample dried at 70°C/12 h.

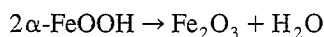
In the 700–820°C interval, a second weigh loss of the order of 5% is observed due to the decomposition:



Furthermore, there is a progressive loss of weight until high temperatures with a small inflection point to 1100°C which can be due to the decomposition of the CaSO_4 content in the sample.

Concerning the DTA curve, the first endothermic peak until 180°C indicates the loss of water, beginning below an exothermic band that ends at 600°C with a clean-looking exothermic peak that corresponds to hematite crystallization. An endothermic peak to 768°C corresponds to the decomposition of iron sulphate and the corresponding weigh loss in the TG graph. Below, a continuous endothermic descent indicates the existence of a small glass proportion formed by the impurities of the goethite sample.

Fig. 6 shows the relative contraction with temperature that was found for a pressed sample of goethite and observed by heating microscopy. It is proven that there do not exist considerable contractions until 550°C. After this temperature, there exists a progressive contraction that arrives at values of 80% to 1400°C. These high contractions are due not only to the loss of hydrogen and oxygen in the transformation:



that would suppose a 36% in weight of theoretical loss, but also to the phase transformation goethite → hematite, to the progressive SO_2 loss due to the decomposition of the high-temperature sulfates and finally, to the sintering of a vitreous phase with the SiO_2 , Al_2O_3 , CaO , PbO and ZnO impurities. Thus, in the case of a goethite mud desiccated and treated at high temperatures, all the factors that affect the contraction act in this case to increase the volume reduction of the sample with heating treatment. If goethite is used as raw material to produce glasses and glass ceramics, that is the case of present research in progress [14], the contraction does not affect the process of moulding, since at the melting temperature there has been reached practically the maximum contraction and this must be only taking into account in the filling of the crucibles.

4. Conclusions

The original goethite red mud sample has a humidity content between 44 and 47% and a mean density of 3.77 g/cm³, 80% of the sample having a smaller size than 23 μm. The results of chemical and mineralogic analyses have demonstrated that there does not exist a difference concerning the composition and the present crystalline phases, between the total sample of goethite and each one of the fractions obtained by separation in cyclone. Fe_2O_3 , ZnO , PbO and SiO_2 represent the oxide majority components and goethite, maghemite and magnetite the principal present crystalline phases. Concerning its microstructure, the sample of goethite is constituted by smaller particles size to 0.1 μm, agglomerated until grain size close to 1 μm. Concerning the DTA curve, an exothermic peak at 600°C indicates the hematite crystallization, followed by an endothermic peak at 768°C which corresponds to the decomposition of iron sulphate. Below, a continuous endothermic descent indicates the presence of a small glass proportion formed by the impurities of the goethite sample.

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