Magnetic properties in red mud after thermal treatment

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Red mud is the waste of the Bayer technique, concerning the production of alumina out of bauxite ores. Red mud is an industrial waste and therefore the development of possibly useful products is always an interesting task in waste management. In this report, a pyro-metallurgical process is presented according to which the red mud may be transformed into magnetic powder, with relatively acceptable characteristics.

1. Introduction

Red mud is a by-product or waste of the Al_2O_3 production from bauxite according to the Bayer technique. The principle of this method is the chemical reaction of NaOH with bauxite ore, resulting in AlOH and red mud. Bauxite ores are hammered in order to homogenize their powder size before reacting with NaOH. Red mud, being the waste of bauxite is enriched in all other oxides and substances existing in bauxite. Thus it mainly includes Fe_2O_3 in the form of hematite, CaO and SiO_2, TiO_2 in the form of anatase and other oxides [1]. About 700 thousand tones of red mud are produced in Greece every year and they are treated as wastes. Taking into account that Greece holds the 4-5% of global Al_2O_3 production, it can be assumed that more than 14 million tons of red mud per year is produced and is regarded as an industrial waste. Therefore, it is always an interesting task to try to develop by-products out of the red mud.

Several techniques have been used up to this moment for this purpose. The first attempts have been realized towards the usage of red mud in brick manufacturing [2]. A severe disadvantage of such procedure is the alkalic nature of the brick, since red mud includes Na^+ cations, thus affecting the mechanical and thermal properties of the manufactured bricks. A solution to that may be the inclusion of a small percentage of red mud, of the order of 4-7% into the raw materials for brick manufacturing. Another use has been the inclusion of red mud in the raw materials for cement manufacturing [3]. This has the advantage that the quality of cement may be improved due to the presence of ferrous substances in the cement, thus improving its mechanical properties. Another promising idea up to this moment has been the pyrometallurgical reduction of the red mud in order to produce pig iron and thermo-insulating glassy products [4].

Targeting to develop an industrially simple method to use the red mud waste, we have investigated the magnetic properties of the heated material [5]. In this paper we investigate the magnetic properties of the thermally treated red mud samples, in order to allow for its use on magnetic applications. The experimental procedure is presented next with a discussion concerning the possible use of such a pyrometallurgical method.

2. Experiment

Several red mud samples have been tested in terms of structure and phase transformations. X-ray diffraction (XRD) and scanning electron microscopy (SEM) have been used in order to determine the nature and size of the coagulated powders. A typical XRD response is illustrated in Fig. 1, illustrating the presence of salts and oxides of Fe, Al, Ti, Si, Ca and Na. A typical SEM micrograph of red mud powder is illustrated in Fig. 2. EDAX analysis in these powders illustrates the presence of the same types of oxides and salts.
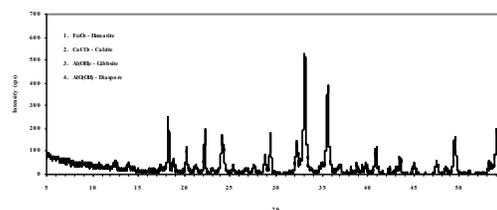

Fig. 1. X-ray diffraction pattern of Red Mud from Pechiney.
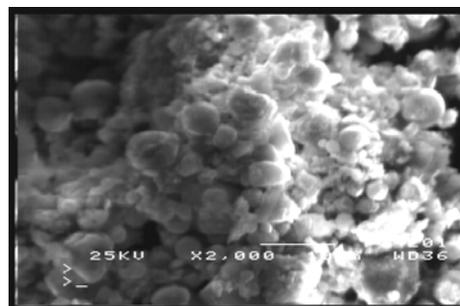

Fig. 2. SEM micrograph of red mud.

Before any thermal treatment and magnetic measurement, the phase transformations with respect to temperature are worth investigating. For this reason differential temperature analysis (DTA) has been performed. For industrial applicability of the presented results DTA studies have been performed in inert atmosphere. Fig. 3 illustrates the DTA response of two different samples of red mud, illustrating possible phase transformations in ~500 °C and ~750 °C. The third phase transformation observed in ~1300 °C is considered as not-usable due to the high thermal energy required. The phase transformations of the red mud might be interesting in the magnetic properties of the red mud, which have been under investigation. Therefore, red mud samples have been heated in 300 °C, 400 °C, 500 °C, 600 °C, 700 °C and 800 °C and their XRD response has been determined, in order to observe phase transformations of the ferrous susbstance, i.e. the hematite coagulated powders. A percentage of Fe and Fe_3O_4, increasing with temperature was observed in X-ray diffraction. Above 600 °C the γ-Fe_2O_3 phase was present. In 800 °C almost only the γ-Fe_2O_3 phase (a magnetic oxide) was present.
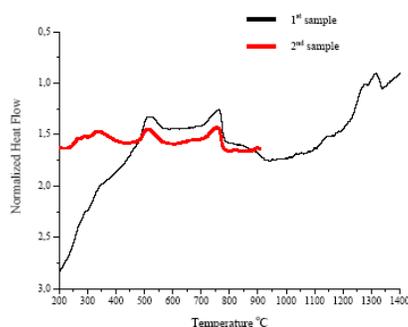

Fig. 3. DTA analysis of Red Mud sample, illustrating the phase transformations.

These experiments have been verified by thermo magnetic measurements in vibrating sample magnetometer (VSM) in inert atmosphere for industrially applicable results. With such the magnetic moment dependence on temperature of the under test substance is determined. A first thermomagnetic response was realized for temperatures up to 500 °C. A repeatable but small increase of magnetization was observed in 500 °C. No significant magnetization changes were observed for temperature increase before 500 °C. Above 600 °C the magnetization was increasing significantly.

Thermomagnetic measurements in 300 °C, 400 °C, 500 °C, 600 °C, 700 °C and 800 °C are illustrated in Fig. 4, in which it is observed that the magnetization values of the red mud is about the 35-40% of the magnetization of the γ-Fe_2O_3 [7]. Taking into account that the 35%-40% of the red mud is a-Fe_2O_3 the experimental data of Fig. 5 prove the statement that the transformation of a-Fe_2O_3 iron oxide into a magnetic phase takes place in 800 °C (or more precisely above 750 °C as the DTA results suggest).
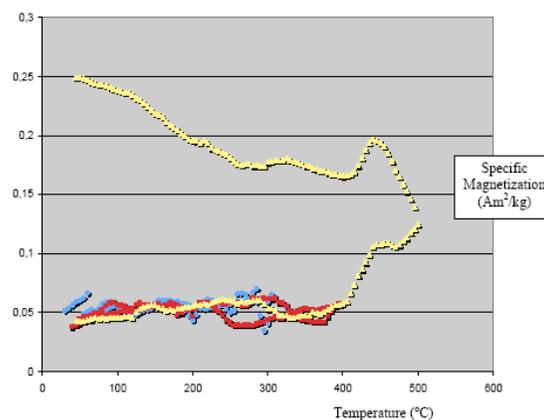

Fig. 4. Thermomagnetic measurements up to 500 °C.

3. Discussion and conclusions

A theoretical model, based on iron phase transformations upon heating is proposed, allowing for the comprehension of the induced bulk net magnetization during heat treatment. Specifically, it is well known that Fe_3O_4 can be obtained either by partial oxidation of FeO, or more conveniently by heating Fe_2O_3 at high temperatures in an inert atmosphere. The latter reaction is completed at temperatures about above 1400 °C, and in reality represents a typical pyrolysis (or decomposition) procedure, which can also be realized as an indirect reduction method.

However, as was depicted by specific magnetization measurements the afore-mentioned reaction can well initiate, at low yields, even at temperatures around 450 °C. This means that in the temperature range investigated, a small proportion of the fundamental iron phase (hematite) existing in red mud has transformed into ferrite.

Between 450 and 575 °C, most of the ferrite phase, which is a mixed oxide of the inverse spinel structure constituting of FeO and Fe_2O_3 oxides at 1:1 ratio, participates with only its Fe(+2) part in another reaction. Below 575°C, FeO is unstable towards disproportionation into Fe and Fe_3O_4 and can be obtained as a metastable phase only if cooled rapidly. Thus, one should expect that below 600°C, the phases present are:

450<T<575 °C

a) Initial ferrite, which not transforms into any other phase.
b) Metallic Fe, being ferromagnetic.
c) Ferrite, which arises as a byproduct.
d) Hematite, arising from the non-participating part of the initially transformed spinell ferrite as well as from the part that was not successfully subjected to pyrolysis.

575<T<600 °C:

a) Initial ferrite, which not transforms into any other phase.

b) Hematite, arising from the part that was not successfully subected to pyrolysis.

It must be addressed that the possibility of metallic Fe occurrence is viable only below 575 °C, as the mechanism previously mentioned suggests. The existence of the Fe phase beyond this temperature and over the Curie point (768 °C) would imply the onset of a paramagnetic behavior, which would be accompanied by a reduced increment of the measured net magnetization. The previous assumptions can be readily justified by the hump of the bulk red mud magnetization curve arising at around 600 °C.

At temperatures above 600 °C, the ferrite phase is no longer stable and transforms rapidly into γ-Fe$_2$O$_3$ (maghemite). The latter is the only ferromagnetic phase present until 800°C, which was the upper limit of our temperature measurements. Since the heat treatment took place under an inert atmosphere, maghemite is thermodynamically stable and cannot further transform into α-Fe$_2$O$_3$ (hematite). Obviously, in this temperature region a non magnetic phase (initial hematite) is also present, arising, as previously, from the part that was not successfully subjected to pyrolysis.

Since maghemite is a weak ferromagnetic (or ferrimagnetic) material in comparison with ferrite, one should expect a reduction of the net bulk magnetization beyond 600 °C. But this is not completely true, since as the temperature increases the initial hematite pyrolysis ratio also increases, thus contributing in higher ferrite and consequently maghemite yields leading inevitably to a total magnetization increment. In other words, between 600 and 800 °C the amount of the non-magnetic initial hematite phase continuously reduces. This seems to be the critical parameter in determining a usable specific magnetization area of the bulk material. Especially, between 600 and 700 °C, the previous mechanism imposes the maximum effect on the net magnetization, as is depicted in Fig. 5 ($\delta Ms/\delta T_{(600-700 °C)} > \delta Ms/\delta T_{(700-800 °C)}$). The reason here may be a small quantity of the magnetically strong ferrite phase remaining shortly over 600 °C.
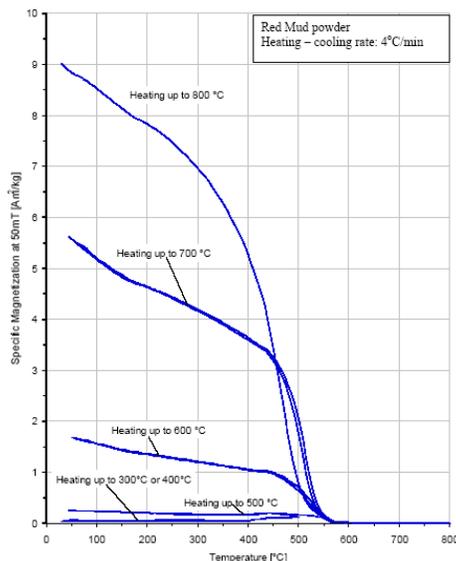
No further measurements exceeding 800 °C were taken, in order for the method to have a viable industrial application, without high energy needs. It can be however expected that until 1400 °C, the net magnetization will continue to rise, but at a reduced ratio since the magnetically weak maghemite phase strongly stabilizes.
It must also be addressed, that, in any case, cooling must also be performed, under an inert atmosphere, so as to prevent phase transformation into α-Fe$_2$O$_3$. Moreover, when the pyrolysis procedure reaches its end, pure ferrite can be obtained from the metastable phase of maghemite by heating in vacuum.

Taking the above into account, it must be concluded that upon heating the net magnetization of red mud's bulk material depends strongly on the dominant phases present at various temperatures. At relatively low temperatures (450<T<600 °C) strong magnetic phases occur and compensate for the reduced pyrolysis ratio of the initial hematite phase. At higher temperatures (600<T<800 °C), hematite decomposition ratio becomes the proposed critical factor, thus compensating for the stabilization of the magnetically weak γ-Fe$_2$O$_3$ phase.

Taking into consideration that the time of the complete phase transformation is important for industrial use of the presented method, time dependence experiments were realized in order to determine the optimum time window for complete a-Fe$_2$O$_3$ into γ-Fe$_2$O$_3$ transformation. Magnetic response dependence of the heated red mud on time is illustrated in Fig. 6, illustrating that 10 minutes in 800 °C may be enough for such transformation.
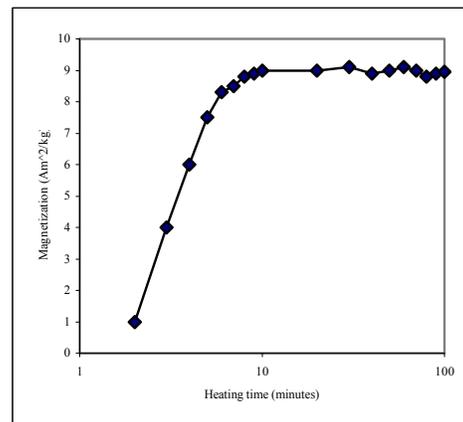

Fig. 6. Magnetic response for red mud samples heated in 800 °C with respect to time.

After heating and transforming the a-Fe$_2$O$_3$ into γ-Fe$_2$O$_3$, the quantitative reception of γ-Fe$_2$O$_3$ may be realized by magnetic separation techniques. Accordingly, the coagulated powders are hammered in ambient atmosphere with no possibility of phase transformation and then a permanent magnet separator can be used for the magnetic separation of γ-Fe$_2$O$_3$. Taking into account that the modern bauxite-alumina factories use pressure filters for the elimination of H$_2$O in red-mud the proposed industrial solution may be as follows: the red-mud is

Fig. 5. Red mud thermo-magnetic cycles up to 800 °C.

driven into pressure filters in order to eliminate the presence of H_2O in it. Subsequently it is driven into 800 °C ovens preferably operated by natural gas, for not more than 10 minutes in order to develop the γ-Fe_2O_3 phase. Inserting the red mud in the oven may follow either a batch or a continuous line type of process. Consequently, the heated red mud is driven into dry hammer systems which are alike (or the same) with the bauxite ones, where the coagulated powders are milled down to the typical 20 μm + 2 μm powder size. Such uniform powder size is easily separated by using permanent magnet separators in ambient conditions. The complete schematic of the procedure is illustrated in Fig. 7.
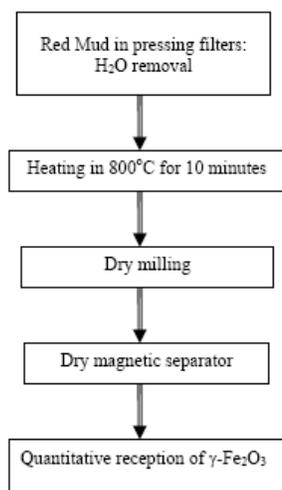

Fig. 7. A possible industrial flow chart for the separation of γ-Fe_2O_3 from the red mud.

Finally, it can be concluded that the red mud can be processed under natural gas heating in 800 °C for 10 minutes wit subsequent dry milling and magnetic separator, from where the γ-Fe_2O_3 can be extracted.

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