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R. Latorre, J. Dufour, J. García, E. Alcalá, C. Negro, et al.. Synthesis of BaFe₁₂O₁₉ by Oxi-Coprecipitation from Hydrochloric Steel Pickling Liquors. Journal de Physique IV Proceedings, 1997, 07 (C1), pp.C1-85-C1-86. 10.1051/jp4:1997123 . jpa-00254903

HAL Id: jpa-00254903

<https://hal.science/jpa-00254903>

Submitted on 4 Feb 2008

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Synthesis of $\text{BaFe}_{12}\text{O}_{19}$ by Oxi-Coprecipitation from Hydrochloric Steel Pickling Liquors

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Abstract. The steel pickling liquor is formed by HCl, washing water and a high content of Fe(II). This liquor is mixed with a Ba(II) solution in a stoichiometric rate to produce a precursor powder to obtain $\text{BaFe}_{12}\text{O}_{19}$. In all cases we obtained a mixture of $\text{BaFe}_{12}\text{O}_{19}$ and $\alpha\text{-Fe}_2\text{O}_3$. The qualitative and quantitative analyses were made by XRD and the magnetic properties were measured by VSM technique. We will report the relation between the oxi-coprecipitation process conditions and the magnetic properties and the role of NaCl during the calcination step. NaCl was formed from dissolution in the oxi-coprecipitation process. NaCl originates structural defects in the powder so, the solid state reaction, during the calcination process, is improved. An excess of NaCl didn't increase the magnetic properties and promoted by-products formation, so the Fe/Ba rate is stoichiometric but calcined products had low magnetic properties.

1. INTRODUCTION.

The steel pickling liquor is a steelmaking wastewater originated for cleaning surface in the last step of steel processing using HCl as pickling agent. It is formed by HCl, washing water and a high content of Fe(II). HCl is previously recovered and recycled to the pickling bath and the effluent, without free acid, is useful to synthesize $\text{BaFe}_{12}\text{O}_{19}$. It is necessary to oxidize Fe(II) to Fe(III) by air as oxidizer agent for precipitation process. This process, called oxi-coprecipitation process, is one of the wet methods for preparing a precursor powder to synthesize by calcination $\text{BaFe}_{12}\text{O}_{19}$. In a first step Fe(II) is oxidized to Fe(III) and, during precipitation of Fe(III) process, a coprecipitation of Ba(II) is produced. In this way, the powder is homogeneous in an atomic scale and, due to the pH where the precipitation is made, the powder is highly reactive, very amorphous and NaCl is present in the powder. NaCl reduces the activation energy of solid state reaction.

2. EXPERIMENTAL PROCEDURE.

The oxi-coprecipitation was carried out using a glass made reactor closed with a lid that has five openings for inserting the diffusor, stirrer, thermometer, condenser and the system for adding the basic agent. The body of the reactor has a side opening for inserting the pH electrode. We prepared in the laboratory a synthetic hydrochloric liquor with 50g/l of Fe(II). This liquor was mixed with a dissolution of BaCl_2 in order to obtain a rate of Fe/Ba stoichiometric to produce the precursor powder. The oxiprecipitation was made, controlling temperature, at 20; 45 and 70°C and pH at 10; 11; 12; 13, using 5 l/min of air with a porous plate diffusor as Fe(II) oxidizer agent. Like basic agent we used Na_2CO_3 saturated dissolution of NaOH 10 M. The reaction was finished when the pH was constant during, at least, 15 minutes. The precipitate was separated from the solution by filtration without washing and dry in an oven during, at least, 48 hours. The rate Fe/Ba in the precipitated was measured by atomic absorption spectroscopy. The crystallinity and the qualitative analysis of crystalline phases were made by X-ray diffraction.

The powder was calcined at 900°C during 3 hours to obtain $\text{BaFe}_{12}\text{O}_{19}$. The qualitative and quantitative analyses were made by XRD and the magnetic properties were measured by VSM technique.

3. RESULTS.

From the solution obtained after filtration we can determine the Ba percentage coprecipitated in the process. These results are shown in table I. In table II are reported the basic agent used during the oxi-coprecipitation process.

Table I. % Ba coprecipitated in the oxiprecipitation process.

pH	20°C	45°C	70°C
10	30,2	23,9	7,4
11	91,8	28,8	33
12	36,8	89,9	88
13	70,8	97,7	98,8

Table II. Volume of NaOH, in ml, needed for the oxiprecipitation process

pH	20°C	45°C	70°C
10	163	170	171
11	188	180	181
12	176	185	237
13	183	507	700

In the qualitative analysis, made by XRD, up to pH 12 there is a crystalline phase of BaCO_3 . That involves a different mechanism of coprecipitation. In all cases NaCl is present and the ferric phases are $\alpha\text{-FeOOH}$, Fe_2O_3 alone or in a mixture [1]. The coprecipitation mechanism is a complex phenomena where superficial adsorption, occlusion and inclusion are present. The inclusion phenomena could be produced with or without removing iron to the dissolution. If Ba is inside the crystal structure it cannot react and cannot originate a crystal structure. If Ba is in the surface, it can react and forms a crystal structure. So, in this way, at low pH, above 12, the inclusion and occlusion phenomena are present and the adsorption phenomenon has no significance. Up to pH 12 the adsorption phenomenon has significance. The substitution effect, removing iron to the solution has more significance at high temperature.

3.1. Ba-hexaferrite formation.

Ba-hexaferrite formation was processed at 900°C during 3 hours. The qualitative and quantitative analyses were done by XRD and the magnetic properties were obtained from their hysteresis loops. Table III shows the obtained results.

Table III. Qualitative and quantitative analysis and magnetic properties of obtained Ba-hexaferrites.

T(°C) pH	20 10	20 11	20 12	20 13	45 10	45 11	45 12	45 13	70 10	70 11	70 12	70 13
%BaFe ₁₂ O ₁₉	----	91,7	5,2	66,0	----	28,7	39,2	----	----	66,8	81,1	----
M _s (emu/g)	3,3	49,2	10,1	25,4	6,9	16,0	17,1	6,7	3,8	25,5	35,4	0,6
M _r (emu/g)	0,2	28,5	0,6	15,4	2,2	7,1	10,0	2,9	0,4	15,0	22,3	0,01
H _c (kA/m)	31	420	26,0	358	101	154	353	222	30	326	375	26

At 20°C and pH 11 the liquor flocculation promotes the adsorption process and the coprecipitation and the magnetic properties are abnormally high in relation to the others. In all cases M_s and M_r are higher when the amount of Ba²⁺ is higher in the precipitate except at 45 and 70°C and pH 13 where the magnetic properties are very low. The reason of that is the great amount of NaCl present in the powder.

3.2. Effect of NaCl.

Some known amounts of NaCl were added in order to study the effect of NaCl in the precursor powder [2-3]. In these samples there are two kinds of NaCl; the first one in the ferrous matrix generated by the precipitation process and the former NaCl added later. The results show that this known amount of NaCl did not affect the reaction extension neither the magnetic properties. We can conclude that NaCl minimizes the reaction temperature due to the defects promoted in the ferrous matrix and not as flux phase. A great amount of NaCl decreases the magnetic properties promoting the formation of intermediate phases.

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