

Short communication

Simultaneous production of impurity-free water and magnetite from steel pickling liquors by microwave-hydrothermal processing

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Abstract

Pickling plants produce large amounts of toxic and hazardous wastes containing heavy metals, thus creating an important environmental problem associated with steel production. This communication reports the use of the microwave-hydrothermal technology to remove metals from pickling liquors and also to produce electroceramics, which results in the simultaneous generation of impurity-free water and value-added materials. The results showed that the microwave-hydrothermal processing was efficient to produce magnetically soft ferrites, as well as to eliminate the heavy metal contamination from the spent liquor.

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1. Introduction

The disposal of pickling solutions is still one of the major environmental concerns of the steel industry. The volume of waste material is considerably high: approximately 60% of rolled steel products, high-grade steel and stainless steels are pickled at least once and the quantity of iron dissolved during pickling accounts for up to 1.2 wt.% of the steel being pickled (Rituper, 1989). The standard practice for the treatment of this liquor is the neutralization and the consequent precipitation of metals, followed by discharge. However, this procedure is usually not sufficient for the purification of the resulting water to an extent that allows its discharge in the environment (Kanari et al., 2001). Also, the obtained products (used in the

treatment of water or as component for animal nutrition) may suffer some market restrictions due to eventual remobilization of the contaminants. After the 1990s, moved by environmental and economic issues, new approaches and methodologies were investigated for the treatment of pickling liquors. These include electrodialysis (Paquay et al., 2000), membrane distillation (Tomaszewska et al., 2001), selective precipitation (Dufour et al., 1997, 2001, 2002; Heras et al., 2004), anion exchange/membrane electrowinning (Csicsovszki et al., 2005), and spray roasting (Kladnig, 2003). Some of these works led to the production of iron salts (chlorides and sulfates) as well as magnetic materials (ferrites). Spinel ferrites are ferrimagnetic materials with general formula AB_2O_4 , which are used as transformer cores in high-frequency power supplies. Among the vast literature dedicated to the study magnetic ferrites, few works have been dedicated to the production of ferrites from wastewaters, with the exception of those by Dufour et al. (2002), López-Delgado

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et al. (1998), López-Delgado (1999) and Latorre et al. (1997), who investigated the production of ferrites from spent acid liquors. Nevertheless, the reported works focused on the production of electroceramics rather than the removal of metals from the aqueous phase to obtain impurity-free water.

The development of new routes for the treatment of solutions or synthesis of materials is driven by the continuing need for fast and energy-efficient techniques. For example, microwave-assisted routes are used in many areas of knowledge in new processes as well as substituting many conventional preparative methods (Adam, 2003). Microwave-based methods are generally much faster, cleaner, and more economical than the conventional practices. Also, new approaches and even unexpected results have increased the interest for the use of microwave energy in many processes involving chemical reactions (Adam, 2003; Jafarifar et al., 2005). Recently, the microwaves were introduced as an innovation in the conventional/autoclave hydrothermal process to produce a wide range of materials for industrial applications. It appears to be a low-energy processing route (minor environmental impact) to clean wastewaters as well as to obtain crystalline and single-phase materials at mild temperatures and pressures with morphology control (Byrappa and Yoshimura, 2001; Palchik et al., 2000; Ku et al., 2002; Dias and Ciminelli, 2003; Liu et al., 2004). Also, an additional advantage of the microwave-hydrothermal process is that a hazardous industrial waste may be turned into a relatively cheap and accessible source of raw material to produce a more valuable product, such as electroceramics, in comparison to the traditional sulfate and chloride salts. Finally, and especially relevant, is the possibility to immobilize hazardous elements present in the effluent solution into the ceramics product. One unique process, or with few variations, can be used to treat pickling liquors from various sources, which is important to reduce capital and operating costs. In view of that, this communication aims to apply the microwave-hydrothermal technology to reduce the content of hazardous metals in spent pickling liquors to an acceptable level and also to produce high-value added materials for technological applications. This is a new approach, important from both environmental and economical points of view, once it combines the pollutants removal from the aqueous phase together with the concurrent production of valuable materials.

2. Experimental

Samples of chloride pickling liquors from local steel industries were analyzed by atomic absorption spec-

trometry (Perkin-Elmer Aanalyst 300), except for C1, determined by ion chromatography (Dionex LC20). The iron oxidation state was determined by titration with $K_2Cr_2O_7$. For each synthesis, 50 mL of solution with approximately 76% of original spent pickling liquor was prepared. Microwave-assisted hydrothermal experiments were performed using a Milestone MLS-1200 MEGA microwave digestion system (2.45 GHz). The system was programmed to work at 1000 W, for 5 min, up to the processing temperature (110 and 200 °C) and maintained at 400 W, for 5 and 60 min (autogenous pressure). The selected pH values were 6, 7.5, 9, 11 and 13 (adjusted with NaOH). The effect of the metals concentration was investigated by dilution of the original pickling liquor at 76%, 38% and 7.6% in a volume basis. After each synthesis, the resultant solution was centrifuged to separate the liquid phase from the solids. The liquid phase was chemically analyzed by induced coupled plasma spectrometry ICP-OES (TJA 61E). The precipitate was washed with hot water and centrifuged three times in order to remove all NaCl formed and dried overnight at 80 °C. Crystalline phases were determined by X-ray diffraction in a Philips PW1830 diffractometer with $CuK\alpha$ radiation (40 kV, 30 mA) and graphite monochromator, from 10 to 100° 2θ at a speed of 0.02° $2\theta/s$.

3. Results and discussion

The chemical composition of the original pickling liquor is shown in Table 1. A list of maximum permitted levels according to the local environmental legislation is also presented (COPAM, 1987). The concentration of most elements, including heavy metals, is quite superior to these limits, especially in the case of Fe, Pb, and Mn, for which the concentrations are many thousand times superior than the maximum permitted levels. This fact shows the importance of an adequate cleaning treatment of the spent liquor before discharge. The effect of pH on the removal of metals from pickling liquors, such as Fe, Mn, Co, Cr, Ni, Cu, Pb and Zn, is shown in Fig. 1. This plot presents the final metal concentration (in a log scale) as a function of the pH selected for the microwave-hydrothermal processing. The results showed that the highest removal of metals from the pickling liquor was obtained at pH higher than 9 for all elements. This result is directly associated with the precipitation of magnetic ferrites and will be better understood after the analysis of the solid phases obtained at these processing conditions. In order to illustrate the effect of the microwave-hydrothermal treatment, Fig. 2 presents a comparison of the metal

Table 1
Chemical analysis of the spent liquor (mg/L)

Element	Spent liquor (mg/L)	Maximum permitted level (mg/L)	
		Class 3 effluent ^a	Discharge (special class) ^a
Fe _T	91,900	5	10
Fe ²⁺ /Fe ^T	0.9	–	–
Cl ⁻	157,300	250	–
Zn	1010	5	5
Ca	290	–	–
Cr ^T	130	0.5 ^b 0.05 ^c	1 –
Mo	4.4	–	–
Co	2.0	0.2	–
V	1.8	0.1	–
Ti	7.0	–	–
Na	730	–	–
As	0.4	0.05	–
P	400	0.025	–
Mn	890	0.5	1
Pb	870	0.05	0.1
Sr	5	–	–
Si	3	–	–
K	94	–	–
Al	25.7	0.1	–
Mg	18.8	–	–
Ni	13.6	0.025	1
B	40	0.75	5
Cd	0.15	0.01	0.1
Sn	2.8	2	4
Cu	10.5	0.5	0.5

^a The least restrictive specification, water not appropriate for human consumption (COPAM, 1987).

^b Related to Cr⁺³.

^c Related to Cr⁺⁵.

concentrations in the original liquor and after microwave-hydrothermal treatment at 110 °C, for 5 min (pH=13) with respect to the levels established by the local environmental legislation for some hazardous elements. As it can be seen, the concentrations were drastically reduced under this processing condition, thus demonstrating the potential of the microwave-hydrothermal technology for the treatment of industrial effluents to obtain impurity-free water. The focus on the aqueous phase represents a new approach, once the previous works emphasized mainly the solids produced.

Now, the effects of the processing conditions on the resulting solid phases will be discussed. Fig. 3 shows the results obtained at 110 and 200 °C, 5 and 60 min and pH 6, 7.5, 9, 11 and 13. The relative amount of the solid phase produced under a given experimental condition was estimated by comparing the relative area below the main X-ray diffraction peak of each phase. Magnetite (M) was found in amounts superior to 25% in all conditions; its relative quantity clearly increased with

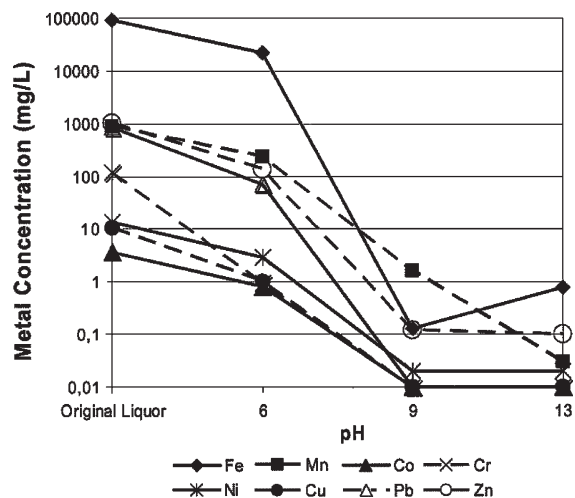


Fig. 1. Selected metals concentration as a function of solution pH after microwave-hydrothermal treatment at 110 °C, for 5 min.

the increase of processing temperature and pH values above 7.5. On the other hand, the content of goethite (G) clearly decreased with pH, while the amount of hematite (H) increased with up to a maximum at pH between 7.5 and 9, decreasing after this pH value. β -FeOOH (A) followed a similar trend, but the maximum was observed at pH 7.5 (no akaganeite was found at pH=13). At 200 °C, magnetite appeared as the main phase in all pH conditions. For processing times of 5 min of processing and pH=13, the only identified phase was magnetite, a well-known ferrous ferrite (Fe₃O₄). For pH values below 11, three other phases were observed: goethite (α -FeOOH), akaganeite (β -FeOOH) and hematite (α -Fe₂O₃). At 110 °C, magnetite is the main phase only for pH above 11, while hematite is the main phase at pH 9. For pH lower than 9, no clear

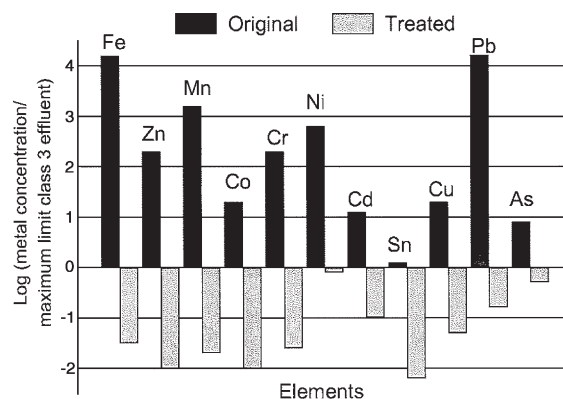


Fig. 2. Ratio between selected metals concentration and the maximum permitted level (Class 3 effluent) for the original liquor and for the liquor treated at 110 °C, for 5 min (pH=13).

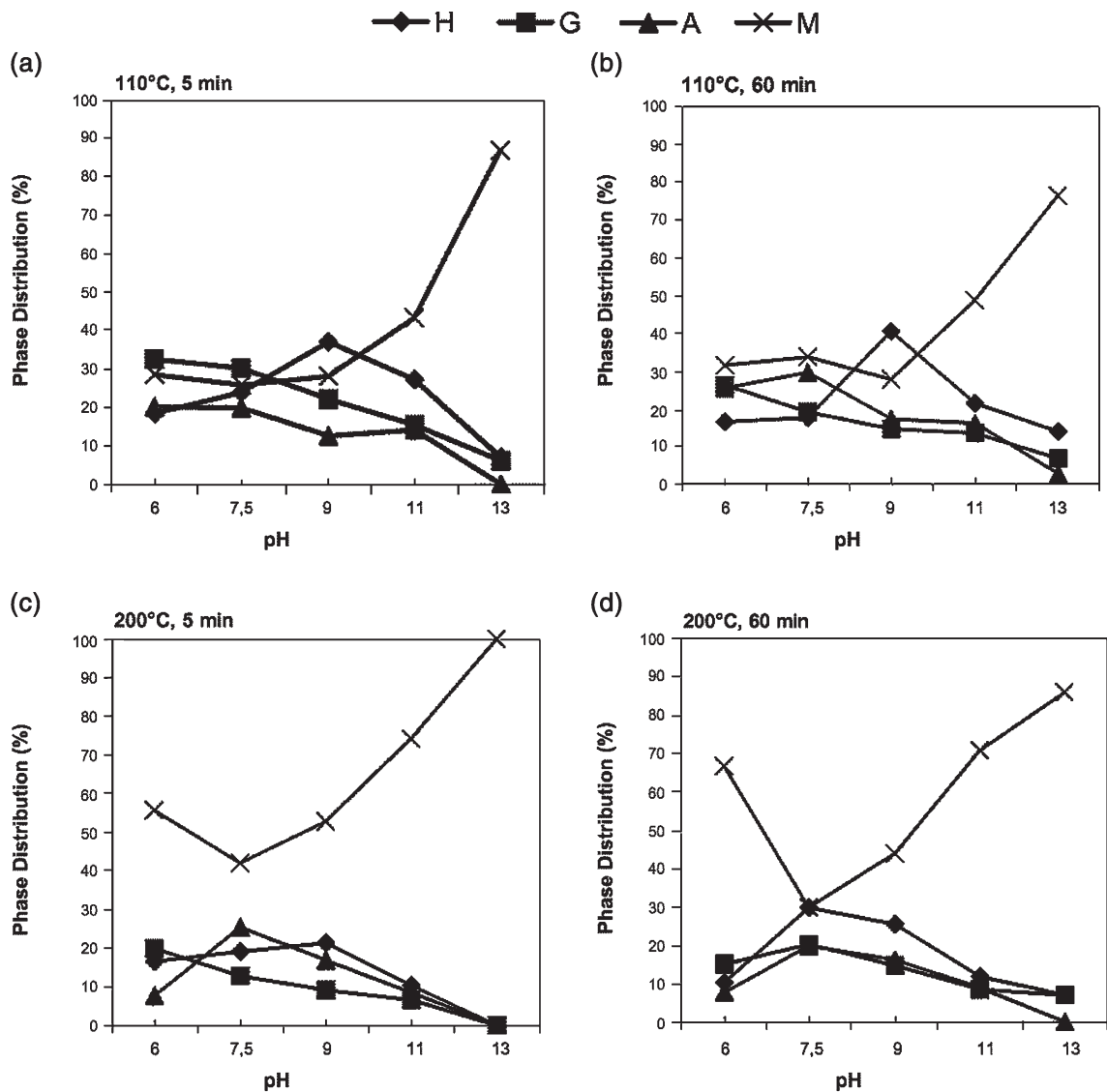


Fig. 3. Relative concentration of each iron oxide phase as a function of pH value for processing temperatures of 110 °C and 200 °C, for 5 (left) and 60 (right) min. The symbols H, G, A and M denote α -Fe₂O₃, α -FeOOH, β -FeOOH and Fe₃O₄, respectively.

preferential phase could be identified. As a conclusion, if the target is the production of single-phase magnetite, strong alkaline conditions are required. Under mild alkaline conditions, a mixture of iron oxides is obtained.

Recently, Wang et al. (1998) and Dhage et al. (2002) studied the preparation and the mechanism of formation of iron oxide phases by decomposition of ferric and ferrous salts in aqueous solutions using microwave radiation. The former verified that pH higher than 10 are necessary to produce stoichiometric magnetite, while pH below 7 favored the formation of α -Fe₂O₃. A mixture of iron oxides was observed between these pH

values under microwave radiation. Similar to the present work, Dhage et al. (2002) showed that the color of the precipitates changed in the sequence light-yellow \rightarrow orange \rightarrow yellowish brown \rightarrow blackish green \rightarrow black. The X-ray diffraction patterns displayed essentially two phases: α -FeOOH and Fe₃O₄ with the transition occurring at pH=8. Differently of our results, β -FeOOH was not observed, probably due to the use of different microwave processing conditions. Microwave radiation appears to provide an efficient source of energy in driving the reaction to occur fast (5 min) and in temperatures as low as 110 °C. It is believed that the

electromagnetic fields into the microwave cavity can promote the migration of the ions, intensifying the diffusion and accelerating the overall reaction (Byrappa and Yoshimura, 2001; Adam, 2003).

Now, the features of the resulting impurity-free water and the solid phases will be compared. A strong correlation between the precipitation of Fe_3O_4 and the reduction of the concentration of heavy metals in solution was observed. Magnetite presents a cubic structure that can accommodate a large number of ions in both octahedral and tetrahedral sites. This offers an opportunity to engineer specific magnetic interactions in the crystal lattice by substituting or incorporating various transition metal cations into the crystal structure, thereby altering the macroscopic magnetic properties. The processing conditions employed in the present work favored the precipitation of Fe_3O_4 in mild temperatures and short period of times (5 min) with incorporation of metal cations into the structure. Thus, the result was the simultaneous cleaning of the aqueous phase from heavy metals as well as the production of an electroceramic. The magnetite obtained can be better described as a complex ferrite of composition $[\text{Fe}, \text{Zn}, \text{Mn}, \text{Ni}, \text{Cu}, \text{Cr}, \text{Cd}, \text{ etc.}] \text{O} \cdot \text{Fe}_2\text{O}_3$, where the bivalent cations are located in both tetrahedral and octahedral sites. Finally, the effect of dilution of the original liquor in the crystalline phases obtained after microwave-hydrothermal processing was studied. As a general trend, the dilution of the original liquor from 76% to 38% reduced the amount of $\beta\text{-FeOOH}$ produced, while the presence of goethite and hematite was still detected. At the highest dilution condition (7.6%), only the single-phase magnetite, with few contaminations, was verified. This result shows that the reduction of the pickling liquor concentration clearly favored the production of ferrous ferrite (Fe_3O_4). Ferrites with different composition can be obtained through the intentional addition of selected chemicals to the original pickling liquors in a way that materials with tailor-made properties are produced.

4. Conclusions

The results showed that the microwave-hydrothermal processing is able to remove elements from pickling liquors, such as Fe, Pb, Mn, Cu, Co, Ni, Zn, Cr, Cd and Sn, mainly at pH higher than 9. Chemical analyses of the resulting impurity-free water indicate its suitability for discharge. Conversely, it was observed that in concentrated liquors, single-phase magnetite (an important electroceramic material) was obtained at pH=13 and processing conditions of 110 °C and 5 min. Lower pH values and temperatures led to the production of other iron oxides, such as goethite, $\beta\text{-FeOOH}$ and hematite.

The relative amount of each phase was found to be strongly dependent on the experimental conditions, notably pH. Thus, the results pointed out to the possibility of the use of the microwave-hydrothermal technology to clean spent pickling liquors from hazardous elements and, at the same time, to obtain a more valuable product.

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