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Magnetic and X-ray Studies of Nanodispersed Magnetite Synthesized from Chrome Containing Galvanic Sludge

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In the current work we discuss the processes occurring along with the temperature treatment of the samples of chromium containing sludge. The results of powder X-ray diffraction and vibrational magnetometry show that magnetite forms in the samples with the increase of the calcination temperature higher than 500 °C. Its quantity increases with the heating, which is clearly visible from the value of saturation magnetization obtained for the samples after various temperature treatments.

Keywords: Magnetite, Electrocoagulation, Calcination temperature, Powder XRD, Magnetization.

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1. INTRODUCTION

Galvanic processes of chrome-, zinc- and copper plating of ferrous metals include operations of prior etching with sulfuric acid and washing with hot and cold water. The same washing should follow the process of plating. The mixture of washings is treated with reducing agents to convert hexavalent chromium to trivalent one. Then, the alkaline environment is created by means of sodium hydroxide, and nanodispersed iron-containing precipitate – galvanic sludge – is formed. It also includes the hydroxides of chromium and other heavy metals with adsorbed sodium sulfate on their particles. As it is shown in [1], galvanic sludge, obtained when the reduction of Cr^{6+} to Cr^{3+} is performed by means of electrocoagulation process, is of great interest from the practical use point of view. Then ions of Fe^{3+} dominate in the galvanic sludge.

We have investigated the influence of heat treatment of chromium-containing galvanic sludge on its composition and magnetic properties to produce nanodispersed magnetite suitable for the synthesis of magnetic fluid.

2. EXPERIMENTAL

A galvanic sludge sample was prepared with its ionic composition modeling precipitate produced in industrial conditions with electrocoagulation method: Fe^{3+} – 100 mass parts; Cr^{3+} – 11,52 mass parts; Zn^{2+} – 0,15 mass parts; Cu^{2+} – 11,52 mass parts. Salts of iron and copper were taken in the form of sulfates. Alkalization and deposition was carried out with sodium hydroxide. The resulting precipitate was dehydrated, dried till constant mass, and then the samples were subjected to heat treatment at a constant temperature, which varied from 20 to 1000 °C. The resulting materials were subjected to radiographic analysis. Their saturation magnetization was determined with the help of vibrational magnetometer.

3. RESULTS AND DISCUSSION

Simultaneous presence of iron, chromium, zinc, and copper ions in the galvanic sludge can influence the course of the ferritization occurring during heat treatment [2]. Impurities affect the crystal-chemical state and thereby the physical characteristics of produced ferrites. In this case it is important to note that, since the radius of Cr^{3+} ion is the closest to the radius of Fe^{3+} (0.063 and 0.064 nm respectively), and the ions of Cu^{2+} and Zn^{2+} are larger (0.072 and 0.074 nm respectively), the probability of penetration of a chromium ion into the forming crystalline lattice of the ferrite-spinel is higher. It is known that in the crystal lattice of such ferrites [2] there are twice as more cations in the octahedral sites than in tetrahedral ones. Ions of Cr^{3+}, which are characterized by the highest energy of preference ($195.5 \cdot 10^{-3}$ J/mol), will be located in the octahedral sites. This means that their influence on the ability of the part of ferric ions to transform into the ferrous ions, (it will be discussed below), can be the most significant.

In the process of calcination of galvanic sludge, dehydration and the formation of oxides along with the presence on the surface of the Cr_2O_3 particles of sodium sulfate (the unwashed galvanic sludge) the following reaction can take place [3]:

$$4Na_2SO_4 + 2Cr_2O_3 + O_2 \rightarrow 4Na_2CrO_4 + 4SO_2$$

The appearance of free electrons initiates the reduction processes in the unit cells, being in the form of a face-centered cube, which leads to the appearance of ferrous irons and creates the possibility of the formation of magnetite.

Diffractometry data (Fig. 1-3) are in agreement with the expected progress of the processes, mentioned above, which takes place during the heat treatment of galvanic sludge.

As one can see from Fig. 1, at room temperature, only Thenardite (Na_2SO_4 with orthorhombic modification) is found in the sample. With increasing calcination temperature starting from 400 °C, phase transition of Na_2SO_4 into hexagonal modification occurs (Fig. 2). The diffraction pattern clearly shows the presence of hematite (Fig. 2). Na_2SO_4 hexagonal modification can correspond to a more active state of this compound from the viewpoint of possibility for the reduction reaction, mentioned

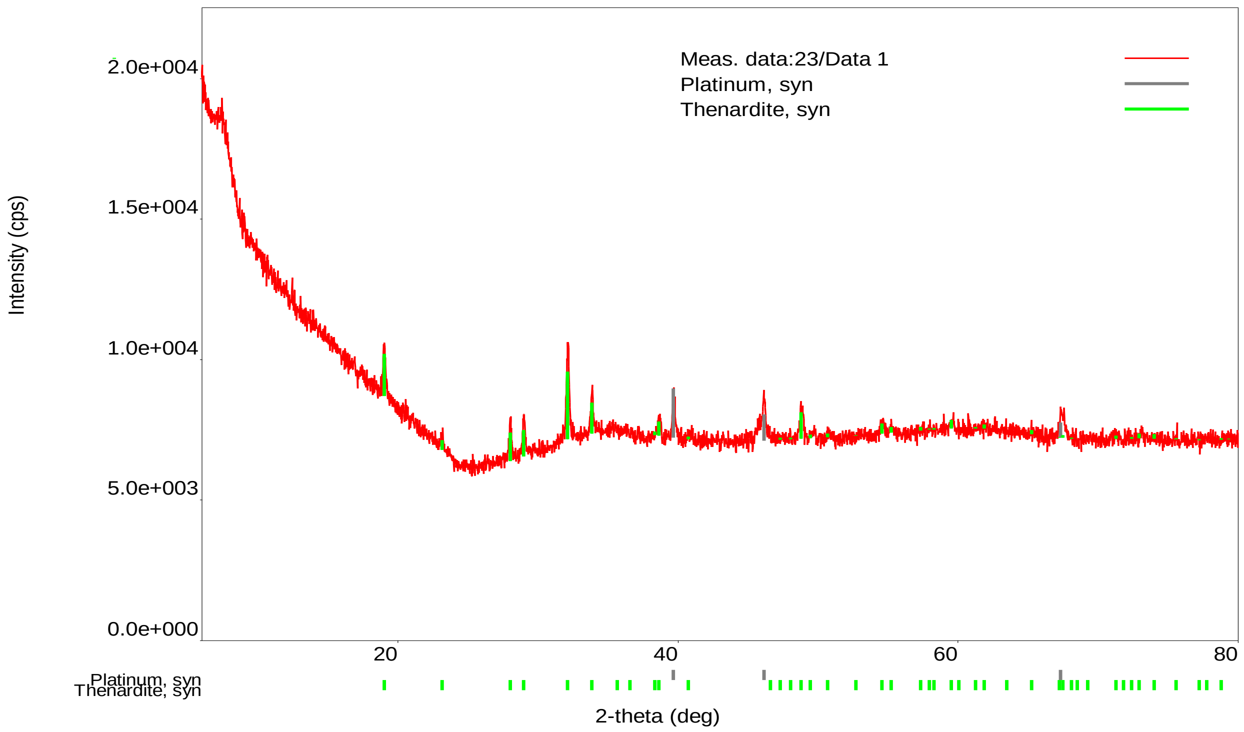

Fig. 1 – Diffraction pattern of the dried galvanic sludge

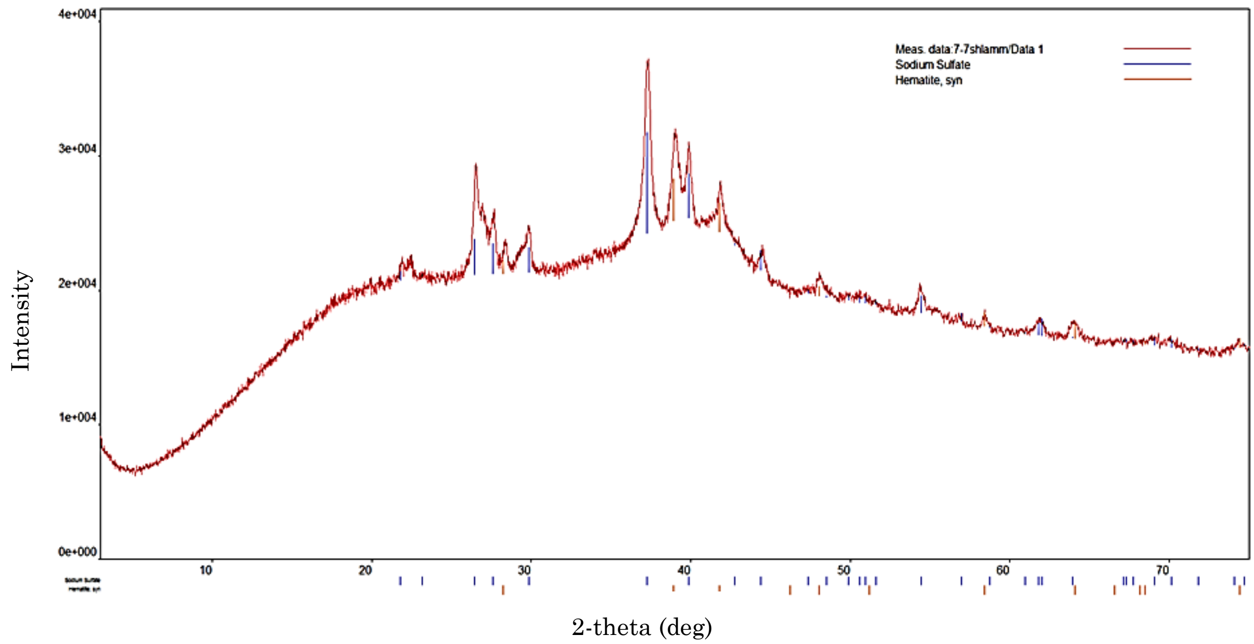

Fig. 2 – Diffraction pattern of a galvanic sludge thermally treated at 400 °C

above and the presence of free electrons. Indeed, when the calcination temperature reaches 500 °C, the peaks, which are characteristic for magnetite, appear in the diffraction patterns (Fig. 3). Their intensity increases significantly with the increase of heat treatment temperature.

The increase of the magnetite contribution in the material resulting from galvanic sludge calcination should lead to an increase of the magnetization of the latter. This is confirmed by measurements of the magnetization, shown in Fig. 4.

It should be noted that the magnetization under the calcination temperature of 1000 °C reaches the values which are characteristic for the magnetite obtained from a mixture of $FeCl_3$ and $FeSO_4$ and with classical co-precipitation method.

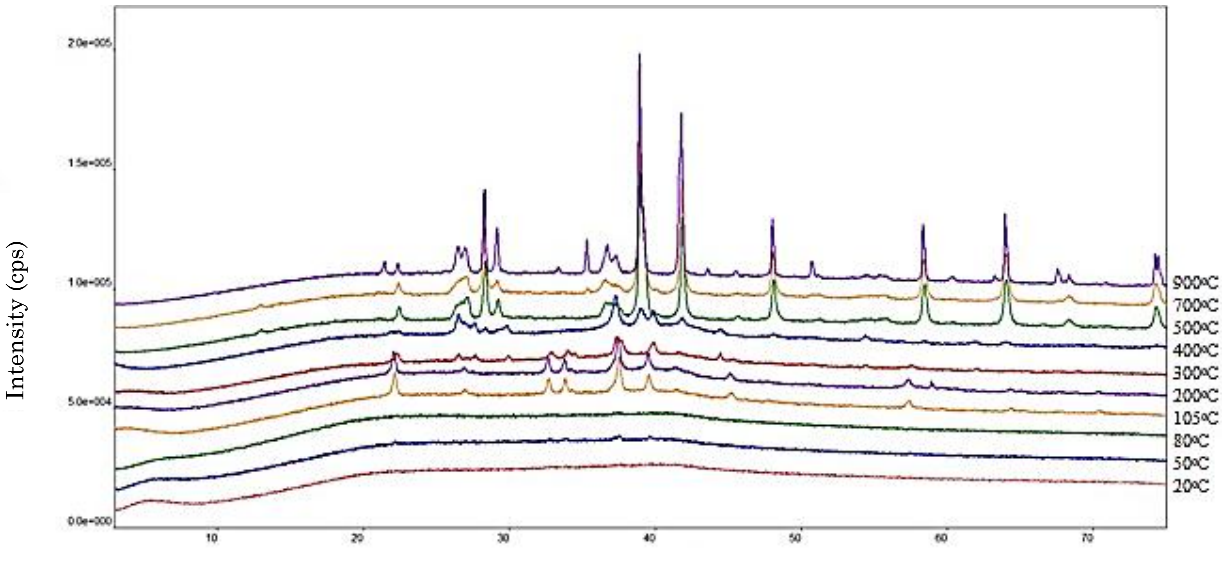

Fig. 3 – Diffraction patterns of samples treated at different temperatures

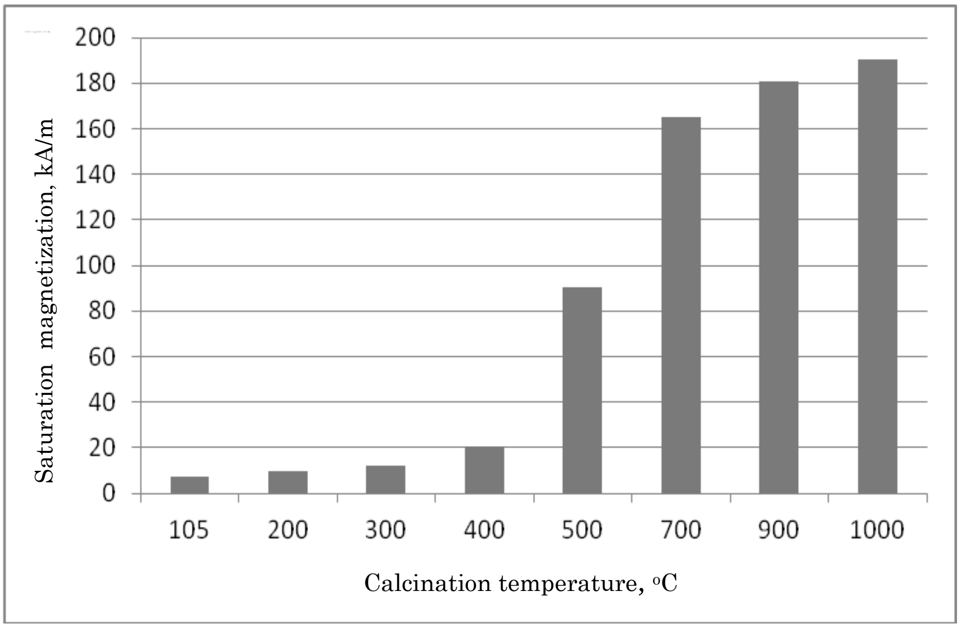

Fig. 4 – Dependence of the saturation magnetization of thermally treated galvanic sludge on the calcination temperature

4. CONCLUSIONS

The results of the present paper allow us to conclude, that the galvanic sludge extracted by means of electro-coagulating purification of wastewater, which contains Cr^{6+}, Zn^{2+}, Cu^{2+} and sulfate ion, can be the raw material to produce the magnetite for the manufacturing of magnetic fluids [4-5].

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