MAGNETIC PROPERTIES OF CHROMIUM-CONTAINING LATERITES

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ABSTRACT

Magnetic properties of chromium-containing laterites from the Philippines and Vourinos deposit, Greece, were investigated. Magnetic properties of the main minerals in the ore, chromite and limonite, were investigated by means of laboratory Franz – isodynamic magnetizer. Differential thermoanalysis at different temperatures and magnetic induction was used, as well as infrared spectroscopy at different wavelengths. Moessbauer spectroscopy was used for determination the ratio of different iron forms in the minerals. The different magnetic permeability of the different minerals in the sample is shown.

The established difference in the magnetic properties of chromium-containing minerals and limonite shows that the ore can be processed by magnetic separators for mechanical separation of the minerals; in suitable magnetic field strength, after selective grinding.

INTRODUCTION

Geological and mineralogical investigations implemented so far have shown that Philippine's laterites, due to their large reserves would be of great importance for the future chromium production (1-5). However, the processing of this kind of ore by mineral processing methods is complicated due to their peculiarities and complex mineral composition. Laterite processability depends mainly on the establishment of the differences in physical and chemical characteristics of the constituted minerals. The difference in the magnetic properties has a great significance.

So far, there are not many investigations on magnetic separation of laterite chromium, because it should be studied the dependence between the magnetic properties and the structure of the minerals; respectively their chemical composition and their behavior in magnetic field

The present study shows the results from the investigations of the magnetic properties of laterite minerals. These results could be useful in magnetic processing of the ore.

METHODS AND EQUIPMENT

To investigate the magnetic properties of the ore a laboratory Franz-isodynamic magnetizer was used. Magnetic permeability of the ore minerals was investigated. The limonite aggregates, obtained atdifferent magnetic induction, were analyzed by means of differential thermoanalysis. Their infrared spectrum was studied too. Moessbauer spectroscopy was applied for the estimation of Fe²⁺ /Fe³⁺ ratio in iron minerals

Equipment used in the experiments

Fig.1 shows the equipment used. This is a laboratory Franzisodynamic-magnetizer, in which the magnetic induction can be determined without levels up to 2 tesla (T). It is used for an investigation of the magnetic properties of the minerals. The separation is performed in a vibrating channel which the length and cross-section have been established preliminary.



Figure 1. Presentation of the forces acting in the classifier

Two forces act in the sorting channel: magnetic force and gravitational force. The magnetic force Fm for a particle with a mass m and magnetic permeability

 $\chi = \kappa/Qq$ acts decreasingly upon the axis of the channel. It can be expressed by the formula:

$$F_{M} = \mu_{0}.\chi.m.H \text{ grad } H, [N],$$
 (1)

Where *m* is the mass $[\kappa g]$; *H* is the field strength,

[A m⁻¹].

Simultaneously acts the friction force F'g:

 $F'g = m.g.sin\theta$, [N]

Where g is gravitational constant, g = 9,81 [m.s⁻²]; θ - is the angle of the slope of the channel.

In the case of equilibrium of the forces it is fulfilled:

and
$$\chi = g \sin \theta \frac{1}{HGradH^2 \mu_0}$$
 (3)

By this formula one can determine magnetic permeability of the mineral grains. Transverse slope θ = 15°, while longitudinal ϕ = 30°. The initial size of the raw materials was 100 – 200 μm . The determination of the materials as magnetic ones was made by microscopic observations.

Magnetic properties of the minerals

Magnetic permeability of the most important minerals

If we place a particle in a magnetic field, the elementary magnets in the substance get magnetized due to the action of the external magnetic field. External magnetic field acts upon the substances placed in it with different force H and proportional magnetization M.

This magnetization can be defined as induced magnetic moment per unit volume. Proportionality constant is determined as magnetic permeability and participates in the formula:

$$M = \kappa_{\mu_0} H, \tag{4}$$

where μ_0 is induction constant ($\mu_0 = \pi 10^{-7}$ Vs/Am).

The quantity k can be defined as a parameter characterizing the magnetic properties of the substances. For different substances it depends on the flux density or the field strength. It can be expressed in terms of:

$$\mu_r = 1 + \kappa \tag{5}$$

Depending on the value of the magnetic permeability the substances can be classified as diamagnetic, paramagnetic and ferromagnetic. It is the difference in the permeability which is used in the process of sorting in magnetic field.

The magnetic permeability of the minerals should be averaged in order to influence crucially the magnetic force of the field. The most suitable magnetic field force for separation of chromite from the vein minerals can be determined on the basis of these results.

MEASUREMENT RESULTS

Fig. 2 displays average magnetic permeability of the major minerals. Magnetite permeability varies within 1.280.000 μ 25.990.10⁻⁹ μ ³/kg. The permeability of partially magnetized magnetites and partially martitized grains is within the same limits.

While needle-shaped ferric goetite and lepidocrite are the main constituents of limonite, showing thus weak paramagnetic behavior and low permeability, the limonite aggregates from laterite areas vary widely and possess relatively high permeability. It can be concluded thereby, that, there are ferromagnetic and ferrimagnetic substances in strongly magnetized limonite aggregates. Hematite possesses relatively high magnetic permeability in comparison to chromite. Accreted to hematite chromite grains have slightly higher magnetization and their separation behavior during classification is very alike.



Figure 2. Total magnetic permeability of major minerals

Magnetic permeability of ilmenite grains varies widely. It depends on the content of Fe_3O_4 and Fe_2O_3 .

The silicates with less iron content such as enstatite and serpentine have lower permeability compared to paramagnetic oxides; iron content in these samples is less than 10 %.

Because vein minerals, such as gypsite and montmorilonite, possess lower permeability than the other minerals, they also do not initiate problems in the process of separation.

Magnetic permeabilility of sulphidic nickel-base minerals, rutile and forms of quartz have been very rarely reviewed.

Magnetic properties of chromite

Chromite mingled crystal, like magnetite, is categorized as ferrimagnetic substance.

Feromagnetic behavior of such ferrimagnetic minerals is exhibited by weak spontaneous magnetization. Chromite contains in larger extent different ions, which are either chemically different or have physically different crystal lattices. Such kind of lattice is presented on fig. 3. The spinel structure forms a dense cubic cell of O² ions in whose octaedric and thetraedric sites adhere cations. Different metallic ions interchange their places due to crystallization difference, so chromite allows the existence of many substituted crystals.

Thirty two oxygen and 24 metallic atoms participate in one elementary chromite cell. For one single junction it is allowed 16 trivalent ions, as Cr^{3+} , Al^{3+} and Fe $^{3+}$ in two different places. Eight atoms are tetraedric of type A, and the remaining eight atoms, such as Fe, Mn and Mg are of type B. The dipoles of these 16 trivalent ions compensate their distribution in the crystal. Eight divalent ions, such as Fe²⁺, Mn²⁺ and Mg²⁺ occupy the remaining sites of B type and they contribute for the magnetization of chromite spinels. Such orientation of magnetic moment in solids is determined as antiferromagnetism.

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The spontaneous magnetic moment of chromite can be described by its own from the divalent metallic ions. As a rule, metallic atoms ordered in antiparallel way exhibit paramagnetic behavior in magnetic field.

Based on these theoretical observations, magnetic properties of chromite vary depending on the mineral structure and the chemical composition.



Figure 3. Perspective drawing of spinel structure

Microscopic study shows that chromite grains are frequently accreted with vein minerals. Because the vein mineral in most of the cases have high iron content, they can influence the magnetic properties of chromite grains. Mass distribution of some minerals in magnetization depends on the magnetic induction. As-used laterite and primary chromite ores originate from alike deposits. Their heavy mineral concentrates were processed by sorting in classifier. During the separation, the cross slope of the classifier was 15^o and longitudinal slope 30^o. Table 1 shows that the observed laterite chromites are more strongly magnetized in comparison to the primary ores. In magnetic induction of 240 mT the magnetization of the laterite ore is around 33.11 %, while the magnetization of the primary chromites is only 4.4 %. The primary ore is magnetically separated mainly in the 329-480 mT limit.

Table 1. Magnetically separated rudimentary and laterite chromite, limonite aggregates and silicates, depending on magnetic induction

Magnetic induction, mT		Weight par	rt,%	
	Primary chromite	Laterite chromite	Limonite aggregate s	Silicate s 0.2 00.8
80	0.2	13.5	2.5	
80-160	0.6	12.4	17.6	
160-240	3.6	7.2	29.3	
240-320	5.4	19.6	33.7	
320-400	59.8	40.1	15.6	
400-480	29.1	6.7	1.2	0.2
480	1.3	0.5	0.1	99.8
	100	100	100	100

The different magnetized areas of the laterite chromites (ρ > 4,19 g/cm³) were analyzed chemically (table 2 and 3). It was found that the increasing magnetic induction of FeO decreases significantly, while the contents of Cr₂O₃, Al₂O₃ and

MgO increase. In magnetic induction of 480 mT, ironcontaining silicates separate, thus Cr₂O₃ content decrease.

It is found from the results that the laterite mass of weakly magnetized chromites has accreted to strongly magnetized minerals, such as magnetite, maghemite and other unknown minerals, which could not be identified by means of microscope. In order to determine the influence of the chemical composition upon magnetic properties of chromite, chemical experiments with short induction intervals of 15 mT were conducted. In increasing magnetic induction FeO content decreases in general, while MgO content increases. Furthermore, oxide content, such as Cr₂O₃ and Al₂O₃, varies widely in all classes. This means that these paramagnetic components of the substance contribute in a low degree to the magnetic moment, therefore, their influence upon magnetization is not significant.

It is known that the spontaneous atomic magnetic moment depends on the number of electrons in 3d and 4f layers. Manganese which might have 4 or 5 electrones in its d layer could contribute crucially for the overall magnetization. Since MnO content is very low in all classes, varying between 0.06 and 0.1 %, manganese magnetic moment is irrelevant to the overall magnetization of chromite. Four electrons in d layer in iron are crucial for the magnetic moment. Elements like titanium do not influence the overall magnetization.

Magnetic properties of the limonite aggregates

Most of the mineralogical studies upon mineral processing of natural iron oxide, respectively iron hydroxide have been made by means of x-ray diffraction analysis, and differential thermoanalasysis (DTA). They show, that the ore contains almost all, so far known crystallographic, iron oxide-base and iron hydroxide-base minerals. There are even oxides without OH-group (α - Fe₂O₃), hematite, and maghemite (γ - Fe₂O₃) as well as oxides which contain OH-group, such as goetite (α - FeOOH) and_lepidocrite (γ - FeOOH). The remaining part of the oxides is x-ray amorphous.

The conditions of ore formation, such as climate, Eh and Ph values, primary rocks, are factors, on which depend the type of bond in iron oxides, respectively hydroxides. The limonite aggregates shown on fig. 2, consisting mainly of iron hydroxides, exhibit widely varying magnetic permeability in magnetic field.. This hinders the application of magnetization in mineral processing of chromite from laterite soils.

Different metals could be found in the limonite aggregates. At first, it was analyzed the chemical composition of limonite aggregates, magnetized in a different degree. The contents of Fe, Cr, Mn, Ni and Co, which influence the magnetization of the aggregates were measured (table 4).

It could not be proved, that there is a connection between the magnetization, and Ni and Co content which would lead to ferromagnetic properties of the substances. Ni content varies between 0.3 and 0.6 %, while Co content between 0.02 and 0.05 %.

The different content of chromium and manganese does not affect the overall magnetic moment. Cr content varies between 0.8 and 1.2%, while Mn content between 0.2 and 0.4 %.

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There is dependence between magnetization and iron content. In increasing magnetic induction of separation, iron content decreases from 57.4 to 39.2 %. This shows possible presence of iron minerals (magnetite, maghemite) in strongly magnetized limonite aggregates. In strongly magnetized

aggregates, separated in magnetic induction varying between 80-95 and 160-175 mT, magnetite could not be identified by means of microscope.

Table 2. Weight distribution and distribution of th	ne metal for laterite	chromite ore of the	magnetic products in
different magnetization ($\rho > 4.1$)			

Magnetic	Woight	ł	Conter	nt,%		Ratio	Cr ₂ O ₃ -
induction mT	%	Cr ₂ O ₃	FeO	MnO	Al ₃ O ₃	Cr/Fe	Extraction %
-40	5.6	15.6	69.4	2.2	4.3	0.20	2.1
40-80	7.9	30.3	42.2	4.3	10.4	0.63	5.6
80-120	8.8	34.2	34.0	6.6	12.8	0.89	7.1
120-160	3.6	36.9	29.2	7.0	13.2	1.11	3.1
160-200	4.9	39.3	27.8	7.9	14.2	1.24	4.5
200-240	2.3	41.3	24.9	8.5	14.4	1.46	2.2
240-280	8.6	43.2	23.5	9.7	14.4	1.62	8.8
280-320	11.0	46.5	21.8	10.3	14.8	1.88	12.1
320-360	16.7	48.7	19.2	10.9	15.0	2.27	19.2
360-400	23.4	49.4	18.5	11.6	15.1	2.48	27.3
400-440	5.2	48.3	18.2	12.7	16.5	2.47	5.9
440-480	0.7	47.7	17.4	13.3	16.8	2.41	0.9
+480	1.3	39.2	18.0	14.5	15.3	2.03	1.2
	100.0	42.4	26.1	9.3	13.8	1.43	100.0

Table 3. Chemical composition of laterite chromite for specific magnetic products

Magnetic induction	Content, %				
mT	Cr ₂ O ₃	FeO	MnO	Mg	Al ₃ O ₃
160-175	47.5/53.3	23.0/23.7	0.09/0.10	7.6/8.2	15.7/21.
240-255	41.1/58.5	21.1/21.6	0.06/0.08	9.5/10.1	11.1/27.
320-335	44.0/56.8	18.6/19.3	0.06/0.07	11.8/12.3	12.0/25.
400-415	39.4/60.3	17.0/17.5	0.06/0.10	13.4/13.8	8.8/30.
480-495	40.6/59.0	14.0/16.5	0.07/0.09	14.3/16.9	9.4/29.

Table 4 Chemical composition of the limonite aggregates in different magnetic products

Magnetic		Content, %				
induction mT	Cr	Fe	Mn	Ni	Co	
80-95	0.9	57.4	0.2	0.5	0.04	
160-175	1.2	53.8	0.2	0.6	0.03	
240-255	1.1	51.2	0.3	0.3	0.05	
320-335	1.0	47.7	0.2	0.6	0.02	
400-415	0.8	45.4	0.4	0.4	0.04	
480-495	0.8	39.2	0.2	0.3	0.03	

The raw material was investigated for maghemite also. The creation of magnetism can be attributed to oxidation of magnets, heating of lepidocrites or other iron trioxides, such as goetite. All these ways of creation could be observed in the nature. Since maghemite shows exothermic reaction in differential thermoanalysis (DTA), this mineral can be easily distinguished from the other iron minerals.

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Differential thermoanalysis



Figure 4. Differential thermoanalysis of different limonite aggregates, separated at different magnetic induction

Chemically analyzed material was used for this study. Fig. 4 shows DTA curves. It was found that two different endothermic peaks occur in the low temperature region – at 90° C and at 340°C. The first one expresses the release of absorption water, while the second one – the formation of crystalline water and OH-groups in goetite, as well as their transformation to hematite. According to Geit, the exothermic reaction of maghemite occurs in degree of crystallization between 350 and 600°C. The expected exothermic reaction was not found in this temperature interval. This reaction was not observed in higher temperature intervals too.

Infrared spectroscopy was applied to study further the minerals (fig 5). For that purpose, the same material which has been used for DTA, was used. In each of the curves, shown in Fig. 5, one can found infrared absorption of goetite and lepidocrite (fig. 5). The characteristic wave number of goetite – around 904 and 803 cm⁻¹ is measured precisely in each sample. At around 1028 cm-1 wavelength, there is weak infrared absorption, typical for lepidocrite. The characteristic lines of infrared absorption of magnetite and maghemite can not be traced in these spectra. Peculiarity of curves 3-5 are the slightly sharp peaks between 3700 and 3400 cm⁻¹. In wave frequency 1600 cm⁻¹ the absorption could not be unambiguously determined, because different hydroxide minerals are absorbed in this region.



Figure 5. Infrared spectra of different limonite aggregates, separated in different magnetic induction

The results of DTA and infrared analysis show, that the limonite aggregates consists mainly of goetite.

Finally a Moessbauer spectroscopy was applied, to measure Fe²⁺/Fe³⁺ ratio in the iron minerals. In changing the γ - source speed, each sample showed different isometric deviation and different radiation adsorption. The six lines spectrum, necessary for estimation of Fe²⁺/Fe³⁺ ratio could not be observed, meaning that this spectroscopy method is not suitable for determination of minerals in this case.

CONCLUSIONS

The present studies of magnetic properties of chromiumcontaining laterites, incorporating modern and effective methods, show that there is a difference in magnetic properties of chromite and the other basic mineral – limonite.

In suitable magnetic induction, within 320-480 mT, a good separation of these two minerals could be achieved.

The chromite product obtained reaches over 40 $\%~Cr_2O_3$ content, at FeO content around 17 %. These results could be a base for future research aimed at obtaining a chromite concentrate.

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