

M. BROŻEK\*, A. SUROWIAK\*<sup>#</sup>, A. JAROSIŃSKI\*\*

## BENEFICIATION OF CHROMIUM WASTE BY MEANS OF MAGNETIC AND GRAVITATIONAL SEPARATION

### ODZYSK CHROMU Z ODPADÓW CHROMOWYCH Z WYKORZYSTANIEM SEPARACJI MAGNETYCZNEJ I GRAWITACYJNEJ

The paper presents the results of investigations of chromium recovery from the Cr waste mud, originating in the production of sodium dichromate. The differentiation of physical properties of particles of different contents of chromium and magnesium compounds is a premise for the use of physical separation methods. The investigations were performed on 2 waste samples, taken by random from the waste dump. The investigations of magnetic and gravity concentration for sample I and II were made, respectively. The results of screen and float and sink analyses of sample II indicate that it is possible to obtain Cr- and Mg-enriched products by means of a combined method of separation, i.e. hydraulic classification and, next, gravitational concentration on the shaking table. The concept of gravity concentration of the tested chromium waste was verified in the technical scale on multiboard shaking tables. The advantage of these fittings in relation to laboratory conditions is the possibility of separation of discussed waste without previous classification. The longer time of separation on the industrial shaking table as well as the respective amount of water directed to the process together with feed enabled an exact separation of initial material. The obtained concentrate in such conditions contains from 25 to 35% Cr<sub>2</sub>O<sub>3</sub>, depending on the chromium content in the initial waste material. It results from the fractional magnetic analysis of sample I that by means of the magnetic separation it is possible to obtain the magnetic concentrate of Cr<sub>2</sub>O<sub>3</sub> content minimum 20% and, simultaneously, to obtain the non-magnetic product of increased MgO content. The optimum separation conditions regarding the yield and content of Cr<sub>2</sub>O<sub>3</sub> were determined. The highest value of criterion *K* for the grade of the concentrate containing over 20% of Cr<sub>2</sub>O<sub>3</sub> is obtained when the 10 mm diameter balls and the 1150 kA/m magnetic field intensity are applied. The yield of the concentrate equals about 9.5 % and recovery of Cr<sub>2</sub>O<sub>3</sub> almost 22%. In the non-magnetic product the content of Cr<sub>2</sub>O<sub>3</sub> equals 7.74% and MgO 27.36%.

*Keywords:* chromium waste, waste management, gravitational concentration, magnetic separation

W artykule przedstawiono wyniki badań odzysku chromu z odpadowego błota pochromowego powstającego przy produkcji dwuchromianu sodu. Różnice we właściwościach fizycznych rozdzielanych ziaren ujawniające się w zróżnicowanej zawartości związków chromu i magnezu pozwoliły na zastosowanie fizycznych metod rozdziału. Badania przeprowadzono na dwóch różnych próbkach odpadów pochodzących z różnych miejsc składowiska odpadów. Na próbkach tych wykonano badania separacji magnetycznej (próbka I) i grawitacyjnej (próbka II). Wyniki analiz granulometrycznych i densymetrycznych próbki II wykazały, że jest możliwe uzyskanie wzbogaconych produktów w chrom i magnez poprzez zastosowanie kombinowanych metod wzbogacania tj. klasyfikacji przepływowej i następnie wzbogacania grawitacyjnego na stole koncentracyjnym. Koncepcja wzbogacania grawitacyjnego badanego odpadu chromowego została zweryfikowana w skali technicznej na wielopokładowych stołach koncentracyjnych. Zaletą ich w porównaniu do warunków laboratoryjnych jest możliwość rozdziału omawianego odpadu bez wcześniejszej klasyfikacji. Dłuższy czas rozdziału na przemysłowym stole koncentracyjnym, jak również ilość wody kierowanej do procesu wraz z nadawą umożliwiły dokładny rozdział pierwotnego materiału. Otrzymany w takich warunkach koncentrat zawiera od 25 do 35% Cr<sub>2</sub>O<sub>3</sub> w zależności od zawartości chromu we pierwotnym odpadzie. Wyniki magnetycznej analizy frakcyjnej próbki I wykazały, że można otrzymać minimum 20% koncentrat magnetyczny zawierający Cr<sub>2</sub>O<sub>3</sub>, jednocześnie można uzyskać produkt niemagnetyczny o podwyższonej zawartości MgO. Optymalne warunki separacji są zdeterminowane przez wychód i zawartość Cr<sub>2</sub>O<sub>3</sub>. Wyższa wartość kryterium *K* dla wychodu koncentratu zawierającego ponad 20% Cr<sub>2</sub>O<sub>3</sub> uzyskiwana jest kiedy zastosuje się kule o średnicy 10 mm oraz natężenie pola magnetycznego 1150 kA/m. Uzysk koncentratu równa się około 9,5% a uzysk Cr<sub>2</sub>O<sub>3</sub> niemal 22%. W produkcie niemagnetycznym zawartość Cr<sub>2</sub>O<sub>3</sub> równa się 7,74%, natomiast zawartość MgO – 27,36%.

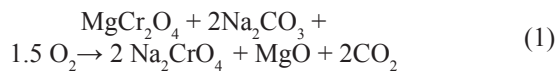
\* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, DEPARTMENT OF MINERAL PROCESSING AND ENVIRONMENT PROTECTION, AL. MICKIEWICZA 30, 30-065 KRAKOW, POLAND

\*\* POLISH ACADEMY OF SCIENCE, 7 WYBICKIEGO STR., 31-261 KRAKOW, POLAND

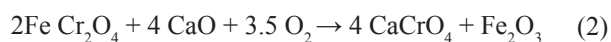
<sup>#</sup> Corresponding author: asur@agh.edu.pl

## 1. Introduction

In general chromium waste having impact on the environment can be divided into two groups: waste generated in the processes connected with chromium ores or their concentrates, e.g. ferrochromium or chromium compounds, belongs to the first group, but the second group comprises the waste derived from the compounds usage, for example the waste generated in neutralization of galvanic sewage, tanning waste and the like. Chromium waste, such as an industrial by-product, is produced in large quantities worldwide and the problem of utilization of these waste products becomes more and more urgent. Analogical problem exists with utilization of red mud produced in the process of alumina production from bauxite (Samal et al., 2013). Twenty per cent of the total amount of chromium waste is generated in chemical industry, mostly in the winning of sodium chromate. This industry consumes about 25 % of chromite raw material for the production of chromic acid for electroplating, pigments and other compounds for, e.g., leather tanning, corrosion inhibitors etc. Sodium chromate is the main intermediate product used in manufacturing of all other chromium compounds. The winning of water-soluble sodium chromate from chromite ores –  $(\text{Mg,Fe})(\text{Cr,Al,Fe})_2\text{O}_4$  has been traditionally achieved by the roasting process of the mixture containing chromite ore, soda-ash and diluent. The type and amount of diluent affect essentially the working load of the blend rotary kiln as well as the quantity of generated chromium waste, the so called post-chromium mud. The overall reactions can be described as follows:



Dolomite or lime are generally used as a diluent which brings about the formation of undesirable calcium chromate. Moreover, adding the diluents to, e.g., calcium oxide fixes it into sparingly soluble in water, according to the equations:



On account of the obtained mud containing up to 2% of Cr(VI), it causes a particular danger because of its carcinogenic influence. Detailed data on the harmful effect of chromium compounds are often published (Papp, 1995; Kowalski, 2002). Therefore the modified technology, which is adopted in some countries, is a much safer method of sodium chromate obtaining (Kowalski and Mazanek, 1998; Tathavadkar and Antony, 2001; Kowalski and Walawska, 2002). At present in Poland the method of sodium chromate production with recirculation of post-chromium mud, generated during the above process, is being implemented (Kowalski, 2002). The quantitative and qualitative characteristic of the solid chromium waste generated in Poland is presented in Kowalski's paper (2002).

Substitution of chromite ore with the post-chromium mud enriched in  $\text{Cr}_2\text{O}_3$  would decrease consumption of raw material and improve energy balance of the discussed process. Such a solution is also essential for the improvement of environment conditions. The comparative study of properties of chromite sintering products, deriving from the industrial process of sodium chromate winning is discussed from the technological and environmental point of view.

Most post-chromium waste is stockpiled while smaller quantities are recycled. Other directions of post-chromium mud utilization and conditions of its safe processing were presented in earlier papers (Jarosiński and Natanek, 1988; Jarosinski and Mączka, 2001). Unfortunately, only in Poland over 3.5 million tons of post-chromium mud have been accumulated during 50 years of production. The total content of chromium compounds in this waste product ranges from 7 to 15%  $\text{Cr}_2\text{O}_3$ . According to Kowalski's investigations (2002) and authors tests it can be stated that optimum concentrates obtained from the post-chromium mud on the way of its upgrading should contain approximately 20%  $\text{Cr}_2\text{O}_3$ . To reach the strategic target of waste elimination, the post chromium mud is used to produce the magnesium sulfate fertilizer. The above mentioned and partially implemented technology of neutralizing of Cr(VI) in the post-chromium mud as well as the recovery of magnesium from this material and application of remaining waste cleared of Cr(III) compounds in the cement industry would decrease the sodium chromate producing waste (Kowalski and Mazanek, 1998; Kowalski and Walawska, 2002).

This work presents the methods of managing the post-chromium mud by means of magnetic or gravity concentration to separate the chromium bearing and magnesium compounds because, as it will be shown further, the first ones are grouped in the magnetic product or in the heavier product of gravitational concentration. This information will be also invaluable to those searching for alternative usage for the products derived from magnetic separation of chromium waste. Moreover, the obtained results should contribute to the improvement of post-chromium mud utilization efficiency with the simulation reduction of industrial waste deriving from chemical industry.

## 2. Materials and methods

### 2.1 Microscopic analysis of chromium waste

The objective of the present study was waste deriving from the winning process of sodium chromate in which diluted dolomite was used. Two samples in independent time intervals from the heap of chromium waste were used for the research.

Microscopic examination of the tested samples was carried out using an optical microscope and scanning electron microscope "JEOL". Microscopic observations allowed the authors to state that basic mass of tested samples was dominated by fine crystalline substance with the grains below 2  $\mu\text{m}$  at full transition of colour between brown and grey. In the mass of samples there were also small independent grains as well as microcrystalline aggregates. In Figs 1 and 2 microscopic images of tested samples are presented.

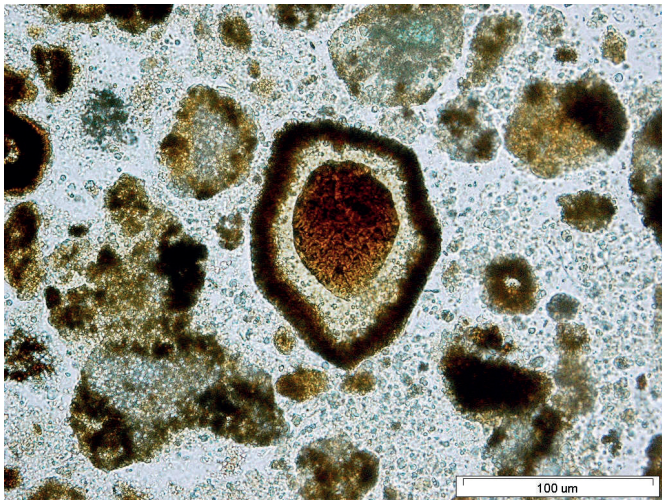


Fig.1. The micrograph of sample I, 1 nicol (grains of brownmillerite, outer built from brownmillerite and zone between them – periclasite)

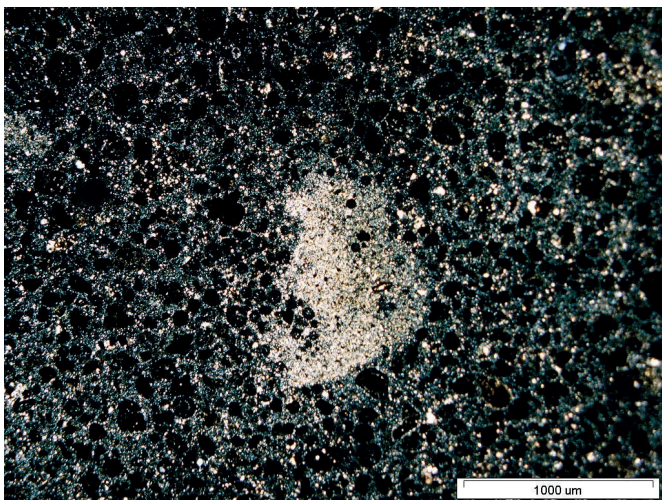


Fig.2. The micrograph of sample II, x nicol (grains of calcite, dark aggregates around calcite – brownmillerite)

The presence of a colourless, turning into grey, isotropic periclasite of high refractive index was observed. The large grains in red-brown shades as anisotropic brownmillerite  $4\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$  were identified. An isotropic chromium spinel, secondary in the tested samples,  $(\text{Fe},\text{Mg})(\text{Cr},\text{Al},\text{Fe})_2\text{O}_4$  is observed. An ink-green non-pleochroic of a very high refractive index and low interference colours occurred rarely. This was calcium oxichromite  $9\text{CaO} \cdot 4\text{Cr}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$  which occurred in fine-crystalline aggregates. The size of these aggregates was about 0.05 mm. The periclasite of a more fine-grained character than this phase occurred in the form of independent grains entered in their composition. Among other minerals, the presence of fine grained calcite was stated in the form of round microcrystalline aggregates of about 10–20 μm.

In order to characterize the tested material, the X-ray investigations with the use of the Philips diffractometer system X Pert. X-ray examination allowed also the authors to state the presence of some above phases in the tested samples (Bonarski et al., 2014).

## 2.2 Chemical composition of samples

The analysis of chemical composition of all investigated samples was conducted according to the classical analytical methods. Alkalis were determined with the AAS (Perkin Elmer 370) method.

Chemical composition of these materials were as follows: sample I – 8.62%  $\text{Cr}_2\text{O}_3$ , 8.50%  $\text{Fe}_2\text{O}_3$ , 6.90%  $\text{Al}_2\text{O}_3$ , 23.60%  $\text{CaO}$ , 26.60%  $\text{MgO}$  and 4.70%  $\text{SiO}_2$ , yet sample II – 7.04%  $\text{Cr}_2\text{O}_3$ , 9.75%  $\text{Fe}_2\text{O}_3$ , 10.08%  $\text{Al}_2\text{O}_3$ , 25.58%  $\text{CaO}$ , 28.22%  $\text{MgO}$  and 3.75%  $\text{SiO}_2$ .

The difference in chemical constitution of the tested samples was minor. Larger differences occurred in distributions of content of chromium compounds in respective size fractions (Tab.1). Relatively large chromium content was observed in the finest particles below 0.04 mm in both samples on account of the largest participation of these particles in the total mass of samples (W – denotes yield of size fraction):

TABLE 1  
Size and chemical analysis of samples

Size fraction [mm]	Sample I		Sample II	
	W [%]	$\text{Cr}_2\text{O}_3$ [%]	W [%]	$\text{Cr}_2\text{O}_3$ [%]
+0.5	4.32	11.10	0.81	7.66
0.5-0.3	1.02	12.49	2.96	6.98
0.3-0.2	10.09	11.69	7.20	8.46
0.2-0.1	13.84	10.69	22.16	10.27
0.1-0.075	26.26	10.34	7.39	11.48
0.075-0.04	10.91	8.72	9.97	10.34
-0.04	33.56	5.03	49.51	4.06

It should be assumed that disposal of these particles by means of hydraulic classification leads to improvement of a upgrading effect in the chromium residual part of the material and, on the other hand, causes a loss from 18 to 30%  $\text{Cr}_2\text{O}_3$ . If in sample I average content of  $\text{Cr}_2\text{O}_3$  is equal 8.62%, then after elimination of fractions below 0,04 mm, this content increases to 10.43%, yet in sample II it increases from 7.04 % to 9.97%. In the first case the degree of upgrading is equal to 1.21 but in the second case 1.42. The result can be a premise to apply the hydraulic classification as a primary operation before the main process of upgrading of chromium waste. Table 1 presents size and chemical distribution of the tested samples.

## 2.3 Size analysis of samples

Granulometric analysis of samples was performed by wet screening on set of sieves of mesh: 0.5; 0.3; 0.2; 0.1; 0.075; 0.04. Dry masses of particle fractions remained on sieves were used to calculate and draw particle size distribution curve for which the model relation was fitted by means of Rosin-Rammler-Bennett equation given by the following formula (Niedoba 2013 a, b; Niedoba 2014; Niedoba and Jamróz 2014):



$$F(d) = 100 \left\{ 1 - \exp \left[ - \left( \frac{d}{d_o} \right)^n \right] \right\} \quad (5)$$

where:

$d$  – particle size,  $d_o$  – characteristic particle size, by which screening lower product yield is equal to 63%,  $n$  – parameter of distribution.

Figure 3 shows a graph of the particle size distribution of both samples. The differences in particle size distribution for the tested samples are insignificant. The particle size distribution function is approximated well by the Rosin-Rammler-Bennett equation, according to the equation (5):

$$F(d) = 100 \left\{ 1 - \exp \left[ - \left( \frac{d}{0.0875} \right)^{0.765} \right] \right\} \quad (6)$$

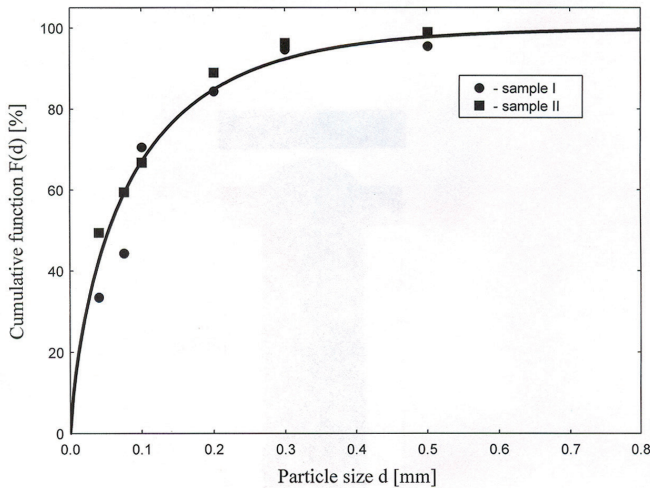


Fig.3. Cumulative distribution function of particle size for sample I and II

The curvilinear correlation coefficient is larger than 0.95. On account of mere differences in chemical compositions of both samples as well as in physical properties; sample I was used to investigate the magnetic separation, but sample II was an object of gravitational concentration investigations.

### 2.4 Float and sink analysis

The preliminary investigation indicated that in heavier fractions such chromium compounds as  $\text{CaCrO}_4$ ,  $\text{CaCr}_2\text{O}_4$ ,  $\text{Ca}_9\text{Cr}_6\text{O}_{24}$ ,  $(\text{Fe,Mg})(\text{Cr,Al,Fe})_2\text{O}_4$  are accumulated, yet in lighter fractions there is periclase, which is the main source of magnesium. In consideration of such compounds distribution, the full float and sink analysis of sample II was carried out. The results of these tests are shown in Figs 4 and 5 which illustrated the relationships of  $\text{Cr}_2\text{O}_3$  and MgO contents as a function of inverse fraction density as well as a distribution function of particle density in the sample, respectively.

Fig.4 presents the cumulative distribution function of particle density in sample II.

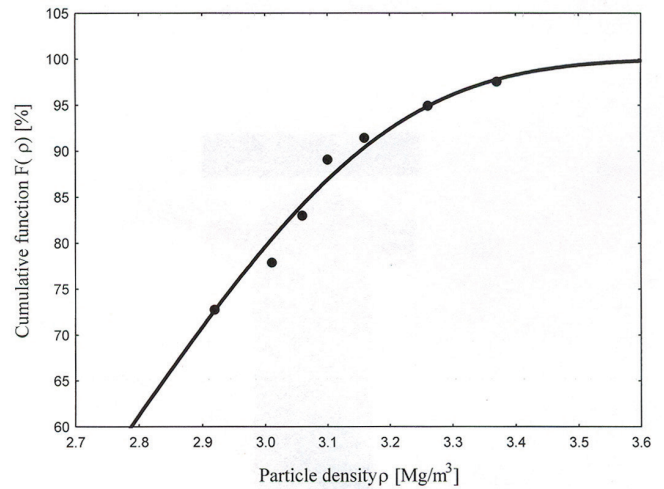


Fig.4. Cumulative distribution function of particle density in sample II

This dependence, according to the particle dispersion model (Brożek, 1995b) is expressed by the Weibull's distribution function (Surowiak and Brożek, 2014 a, b; Surowiak, 2014) :

$$F(\rho) = 100 \left\{ 1 - \exp \left[ - \left( \frac{\rho}{\rho_c} \right)^{k_p} \right] \right\} \quad (7)$$

where:  $\rho_c$  and  $k_p$  are the constants, equal 2.82 [Mg/m<sup>3</sup>] and 7.49, respectively.

The curvilinear correlation coefficient for dependence (7) is larger than 0.98.

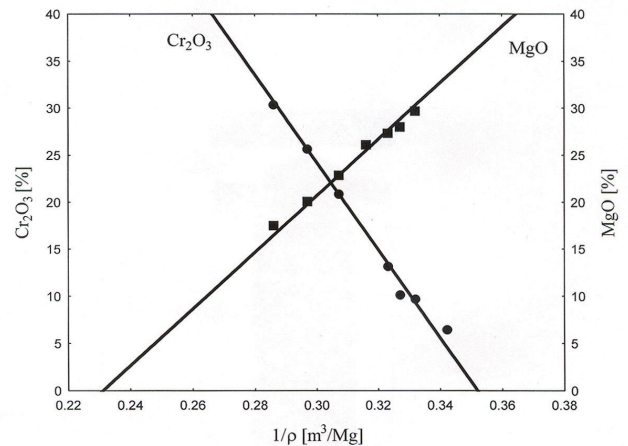


Fig.5. The dependence of  $\text{Cr}_2\text{O}_3$  and MgO contents on the inverse of fraction density

The graph in Fig.5 reveals that with the increase of fraction density  $\text{Cr}_2\text{O}_3$  content increases, on the contrary MgO content decreases. On their basis it may be supposed that by means of gravitational upgrading of chromium waste we can obtain the products differing both in content of chromium and magnesium. The relationships from Fig.4 resulting from the

dispersion model of particle (Brožek, 1995a), analogous to other binary systems approximated the following formulae:

$$\lambda_{Cr_2O_3} = 164.11 - \frac{466.24}{\rho} \tag{8}$$

$$\lambda_{MgO} = -69.37 + \frac{300.12}{\rho} \tag{9}$$

where:  $\lambda_{Cr_2O_3}$  and  $\lambda_{MgO}$  - contents of  $Cr_2O_3$  and  $MgO$  in fraction of density  $\rho$ , respectively.

The calculated regression lines display quite a good compatibility with the test results. This is proved also by a very high linear correlation coefficient  $r > 0.98$ .

From equation (7) for  $\lambda_{Cr_2O_3}$  minimum density of particle -  $\rho_{min} = 2.84 \text{ Mg/m}^3$  can be calculated.

For technological targets a curve of dependence of average  $Cr_2O_3$  content in gravitational concentrate  $G_{Cr_2O_3}$  (in a product of higher density) on density  $\rho$  was calculated and plotted. This relationship is presented in Fig.6 and can be given as:

$$G_{Cr_2O_3}(\rho) = \sqrt{5418.25 - \frac{15625.74}{\rho}} \tag{10}$$

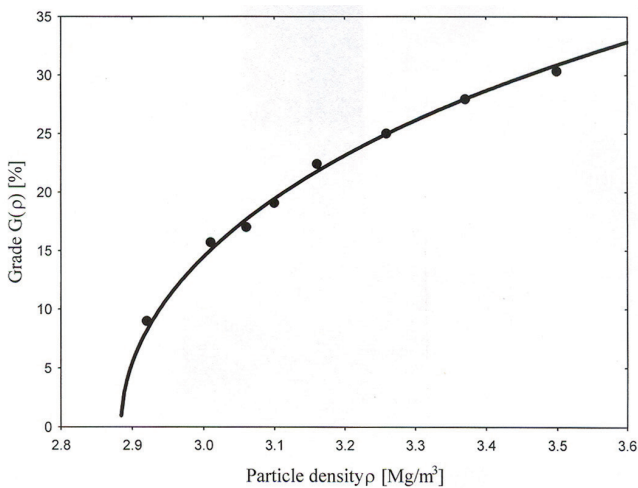


Fig.6. Grade of gravity concentrate versus partition density

From equation (10) the minimum value of division density can be calculated, above which  $Cr_2O_3$  content is at least 20%. This density is equal to  $\rho_r = 3.1[\text{Mg/m}^3]$ .

### 2.5 Magnetic analysis

Analogically as in the gravitational enrichment, it results from the initial investigations of magnetic separation that chromium compositions are grouped in the magnetic product. Therefore the magnetic analysis of sample I was performed. It was carried out applying the magnetic poligradient analyzer. The suspension of very low solid phase contents was separated in laboratory conditions by means of poligradient separator by various values of magnetic field intensity and diameters of balls filling working space between pole pieces of electromagnet in separator.

In each magnetic fraction the content of  $Cr_2O_3$  and  $MgO$  was fixed and specific magnetic susceptibility for each fraction was measured by means of the magnetic balance. The results of this analysis are presented in Figs 7 and 8 in which the dependences of specific magnetic susceptibility upon the content of  $Cr_2O_3$  and  $MgO$  were drawn as well as the cumulative distribution function of specific magnetic susceptibility, respectively.

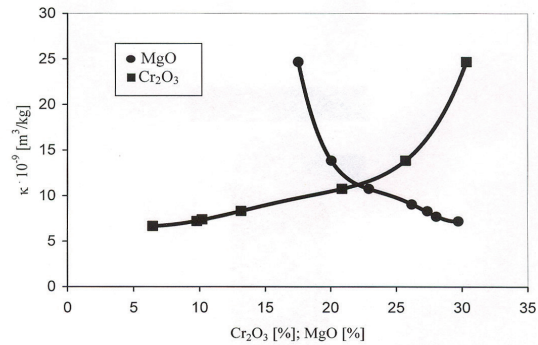


Fig.7. Specific magnetic susceptibility of particles versus  $Cr_2O_3$  and  $MgO$  content

As it can be seen in Fig.7, the content of  $Cr_2O_3$  grows with the increase of specific magnetic susceptibility and, simultaneously, decreases the content of  $MgO$ . So, the compositions of magnesium (periclase) are grouped in the non-magnetic fractions of the lowest specific magnetic susceptibility. This result constitutes a premise to apply magnetic separation to recover chromium from waste and, at the same time, to obtain a product of a higher content of  $MgO$

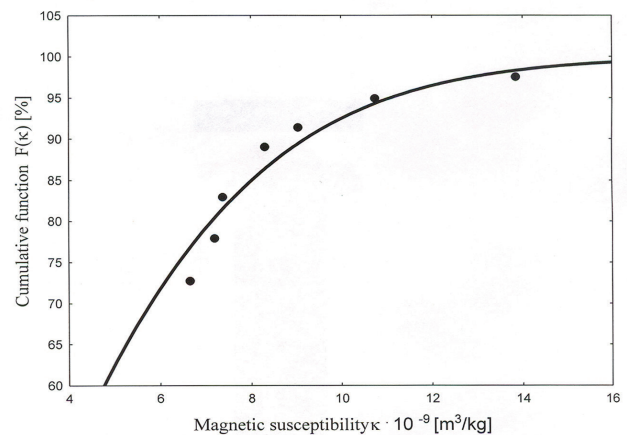


Fig.8. Cumulative distribution function of particle specific magnetic susceptibility in sample I

Figure 8 presents the cumulative distribution function of specific magnetic susceptibility in sample I. This dependence, according to the dispersion model of particle (Brožek, 1995c) and, analogically as the distribution function of density, is

approximated well by the gamma type function, in this case by the Weibull's distribution function:

$$F(\kappa) = 100 \left\{ 1 - \exp \left[ - \left( \frac{\kappa}{\kappa_c} \right)^{k_\kappa} \right] \right\} \quad (11)$$

where:  $\kappa_c$  and  $k_\kappa$  are the constants, equal  $5.07 \cdot 10^{-9}$  [m<sup>3</sup>/kg] and 1.4, respectively.

### 3. Results and discussion

#### 3.1 Gravity concentration of chromium waste

Distribution of chromium content in respective size fractions as well as float and sink characteristics of chromium waste induce to the application of the method of combined classification-gravity concentration. Therefore the investigation of gravitational concentration on the shaking table, after previous desludging in hydrocyclone in order to remove particles below 0.04 mm, was applied. The use of this procedure allowed the authors to obtain two products: underflow and overflow. The first product contained 12.75% Cr<sub>2</sub>O<sub>3</sub> and yield and recovery amounted to 34% and 61.4% accordingly. The degree of upgrading was 1.8. The obtained overflow, as size analysis indicated, included over 99% grains below 0.04mm at weight 66%. Chromium content in this product amounted to 4.15% Cr<sub>2</sub>O<sub>3</sub>. The separation and removal of this product constitutes the essential discharge of gravity concentration process. The underflow from hydrocyclone was directed to gravity concentration on the shaking table. The quantitative diagram of the gravity concentration process is shown in Fig.9.

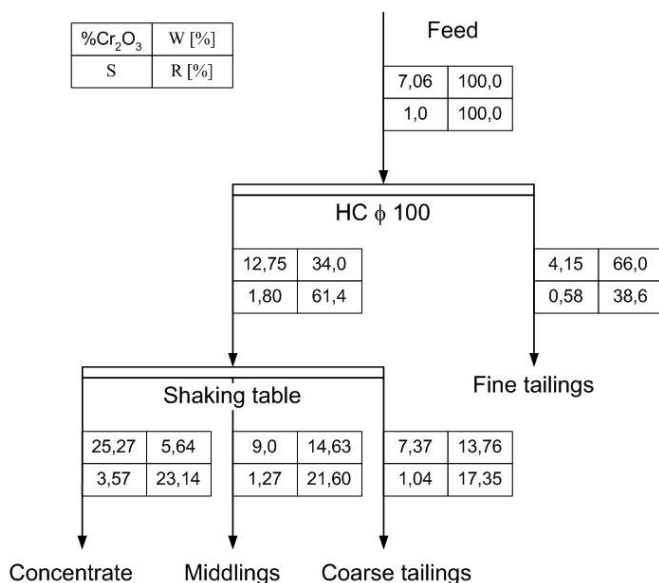


Fig.9. The quantitative diagram of the gravitational upgrading process: S – upgrading rate, W – product yield, R – Cr<sub>2</sub>O<sub>3</sub> recovery

In this case three products were separated from the material feed. The obtained concentrate contained over 25% Cr<sub>2</sub>O<sub>3</sub> with recovery over 23%. These results showed that the chromium waste was amenable to beneficiation by the gravitational way.

The concept of gravity concentration of the tested chromium waste was verified in the technical scale on multiboard shaking tables. The advantage of these fittings in relation to laboratory conditions is the possibility of separation of discussed waste without previous classification. The longer time of separation on the industrial shaking table as well as the respective amount of water directed to the process together with feed enabled an exact separation of initial material. The obtained concentrate in such conditions contains from 25 to 35% Cr<sub>2</sub>O<sub>3</sub>, depending on the chromium content in the initial waste material.

#### 3.2 Magnetic separation of chromium waste

The investigations of magnetic separation of sample I were carried out in the laboratory-type high-gradient separator in which the working space was filled with steel balls. The content of solid parts in the suspension to be separated was fixed and equaled 7 % by weight. The average content of Cr<sub>2</sub>O<sub>3</sub> in the sample was 8.96%. A series of tests were performed in which the ball diameters and the intensity of the external magnetic field were changed. Table 2 presents the test results. The following criterion *K* was used to find the optimum conditions of separation:

$$K = GR = \frac{WG^2}{f} \quad (12)$$

where: *R* – the recovery of Cr<sub>2</sub>O<sub>3</sub> in the concentrate (magnetic product), *G* – grade of the concentrate, *W* - the percentage yield of the concentrate, *f*- the content of Cr<sub>2</sub>O<sub>3</sub> in the feed.

In this criterion, not neglecting the required grade of concentrate, the possibly high recovery of the useful component in the magnetic product is also stressed.

Table 2 lists the percentage yield of the magnetic products *W*, grade of the concentrate and the value of criterion *K*.

The dependence of the content of Cr<sub>2</sub>O in magnetic product on the ball diameter, calculated on the basis of heuristic model of separation is as follows (Brożek, 2003, 2005):

$$G(d) = \frac{100}{1 + 10.6 \exp\left(-\frac{1.59d}{5.56 + d}\right)} \text{ for } H = 750 \text{ kA/m} \quad (13)$$

$$G(d) = \frac{100}{1 + 10.6 \exp\left(-\frac{2.24d}{13.76 + d}\right)} \text{ for } H = 950 \text{ kA/m} \quad (14)$$

where: *d* is given in [mm].

The content of Cr<sub>2</sub>O<sub>3</sub> in the concentrate increases with the growth of ball diameters whereas it decreases with the growth of magnetic field intensity. The change of ball diameter

TABLE 2

Results of magnetic separation

Ball diameter [mm]	Intensity of Magnetic Field								
	750 [kA/m]			950 [kA/m]			1150 [kA/m]		
	W [%]	G [%]	K	W [%]	G [%]	K	W [%]	G [%]	K
15	1.47	22.47	83	2.39	22.75	138	5.36	22.09	292
12,7	4.06	22.15	222	4.63	21.72	244	7.42	21.22	373
<b>10</b>	6.14	21.90	328	8.16	20.28	374	<b>9.44</b>	<b>20.69</b>	<b>451</b>
8	10.92	18.92	436	14.27	17.42	483	21.34	12.13	350

influences more significantly the change of content and yield. It is especially visible if the above dependences are presented in the system of standardized variables:

$$W = 9.77 + 3.58X_H - 6.35X_D \quad (15)$$

$$G = 18.9 - 1.79X_H + 3.38X_D \quad (16)$$

where:  $X_H$ ,  $X_D$  – standardized variables denoting the magnetic field intensity and ball diameter, respectively, and assuming the values +1 and -1.

The regression coefficients at  $X_D$  are almost twice larger than at  $X_H$ . It means that the change of ball diameter influences more significantly the change of grade than the change of magnetic field intensity.

The highest value of criterion  $K$  for the grade of the concentrate containing over 20% of  $\text{Cr}_2\text{O}_3$  is obtained when the 10 mm diameter balls and the 1150 kA/m magnetic field intensity are applied. The yield of the concentrate equals about 9.5 % and recovery of  $\text{Cr}_2\text{O}_3$  almost 22%. In the non-magnetic product the content of  $\text{Cr}_2\text{O}_3$  equals 7.74% and MgO 27.36%. As it results from X-ray analysis, chromium spinels are mainly concentrated in the magnetic product while periclase and calcite constitute the dominating phase in the non-magnetic product. The mineralogical analysis of the concentrate did not reveal major differences in the phase composition in relation to the concentrate of gravity separation.

The screen analysis of separation products for the optimum separation conditions showed that in the magnetic product the yield of size fraction below 0.04 mm equals about 4% whereas in the non magnetic product it is about 46%. Therefore the finest particles find their way to the nonmagnetic product in 99%. Consequently, it would be purposeful to precede the magnetic separation by classification, analogically as discussed before in the gravity concentration.

#### 4. Conclusions

1. As a result of the investigations presented in this paper the conditions of effective enrichment of Cr waste by means of the gravitational and magnetic methods were given. Chromium concentrate of minimum 20%  $\text{Cr}_2\text{O}_3$  content can be obtained by means of the two above separation methods. Due to significantly lower  $\text{Cr}_2\text{O}_3$  content in the particles below 0.04 mm and the passage of these particles to the non-magnetic product, it is recommended to apply hydraulic classification before the process of magnetic

separation. It will improve efficiency and decrease the cost of separation.

2. The 20%  $\text{Cr}_2\text{O}_3$  product can be a substitute of mineral raw materials in the technology of production of sodium chromate. It will decrease disproportions between the demand for chromium-bearing raw materials and the possibilities of their yield. This solution is in agreement with the task concept of this compound, covering the substitution of natural raw materials with Cr waste, applying various recycling methods.
3. The fractions impoverished in Cr and enriched with Mg, similarly as the fine grained waste of the size below 0.04 mm, can be applied to the production of light aggregates, or to the production of magnesium phosphate fertilizer. Consequently, the suggested solution will decrease the rate of Cr ore consumption and decrease significantly the amount of waste, hazardous for the natural environment.

#### Acknowledgements

This work has been supported by grants No. 11.11.100.276 for which we would like to thank the AGH University of Science and Technology

#### REFERENCES

- [1] J.T. Bonarski, L. Tarkowski, S. Pawlak, A. Rakowska, Ł. Major, Archives of Metallurgy and Materials **59**, (2), 437-441, (2014).
- [2] M. Brożek, Archives of Mining Sciences **40**, 63-82, (1995a).
- [3] M. Brożek, Archives of Mining Sciences **40**, 83-100, (1995b).
- [4] M. Brożek, Magnetic and Electrical Separation **6**, 213-228, (1995c).
- [5] M. Brożek, Archives of Metallurgy **48**, 355-367, (2003).
- [6] M. Brożek, The analysis of separation process in magnetic separators on basis of heuristic model of separation. Uczelniane Wydawnictwa Naukowo-Dydaktyczne, AGH Kraków (in polish) 2005.
- [7] A. Ciał, A. Czarski, Archives of Metallurgy and Materials **58**, (4), 1045-1052, (2013).
- [8] J. Greń, Mathematical Statistics. Warsaw, Polish Scientific Publisher (in Polish), 1978.
- [9] A. Jaroński, W. Nataneł, Archives of Environment Protection **3-4**, 185-196 (in Polish), (1988).
- [10] A. Jaroński, W. Mączka., Mineral Resources Management **17**, 89-96 (in Polish), (2001).



- [11] Z. Kowalski, Cz. Mazanek, *Journal of Cleaner Production* **6**, 135-142, (1998).
- [12] Z. Kowalski, *Technologies of chromium compounds*. Cracow, Edited by Cracow Uni-versity of Technology (in Polish), 2002.
- [13] Z. Kowalski, B. Walawska, *Waste Management & Research* **20**, 99-107, (2002).
- [14] T. Niedoba, Multidimensional characteristics of random variables in description of grained materials and their separation processes, *Wydawnictwo Instytutu Gospodarki Surowcami Mineralnymi i Energią PAN, Kraków*, (in Polish) 2013a.
- [15] T. Niedoba, *Physicochemical Problems of Mineral Processing* **49**, (1), 175-188, (2013b).
- [16] T. Niedoba, *Physicochemical Problems of Mineral Processing* **50**, (2), 575-589, (2014).
- [17] T. Niedoba, D. Jamróz, *Archives of Mining Sciences* **58**, (4), 317-1333, (2013).
- [18] J.F. Papp, *Chromium life cycle study*, Information Circular 9411, US Department of Interior, Bureau of Mines, Washington, DC (1995).
- [19] S. Samal, A.K. Ray, A. Bandopadhyay, A review. *Int. J. Mineral Process.* **118**, 43-55, (2013).
- [20] A. Surowiak, M. Brożek, *Archives of Mining Sciences* **59**, (1), 269-282 (2014a).
- [21] A. Surowiak, M. Brożek, *Archives of Mining Sciences* **59**, (2), 553-562, (2014b).
- [22] A. Surowiak, *Mineral Resources Management*, **3**, (1), 105-122, (in Polish) (2014).
- [23] V.D. Tathavadkar, M.P. Antony, A. Jha, *Metallurgical and Materials Transactions*, **32B**, 593-602 (2001).

*Received: 20 September 2014.*