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## Preparation of synthetic carnallite and amorphous silica from chromite beneficiation plant tailings

### Introduction

Chromite concentration plant tailings have an important potential for the production of magnesium based materials because these tailings consist of high magnesium-containing lateritic ores. Besides, contents of the  $\text{SiO}_2$  and precious metals such as nickel and chromium enhance the worth of these type tailings (Top and Yildirim 2015).

Turkey is the sixth largest chromite ores exporter in the world. These ores have been mined from mostly serpentinized ultramafic bodies, discontinuously spread all over the country (Cicek and Cocen 2002; Agacayak et al. 2007; Vapur et al. 2014). Chromite mineralizations, which are one of the most important metallic deposits in Turkey, are clustered in Aladag County of Adana District. Kızılyuksekk deposit of Aladag, where a reserve has 198 000 000 tonnes and 5.37%  $\text{Cr}_2\text{O}_3$  grade, is recently explored by the Mineral Research & Exploration General Directorate (MTA) and this deposit is the largest deposit in the world in terms of ophiolitic chromites (MTA 2015).

Amount of the chromite ores concentration plant tailings processed by 7 plants in this area from 2004 to 2010 are seen in Table 1. Also the tailings' quantities of the biggest and

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old established 2 plants in Aladag area for the last 10 years is seen in Fig. 1. It is obvious that quantity of the tailings increased with every passing year.

Table 1. Amount of the tailings generated by the mining companies in Aladag by years (metric ton)

Tabela 1. Ilość odpadów wytwarzanych przez firmy górnicze w Aladag w latach 2004–2010 (tony metryczne)

Years	2004	2005	2006	2007	2008	2009	2010	Total
Run-of-mine	187 806	191 075	238 786	366 223	566 324	826 083	1 934 276	4 310 573
Tailings	168 586	170 547	217 482	324 750	501 590	748 997	1 766 581	3 898 533

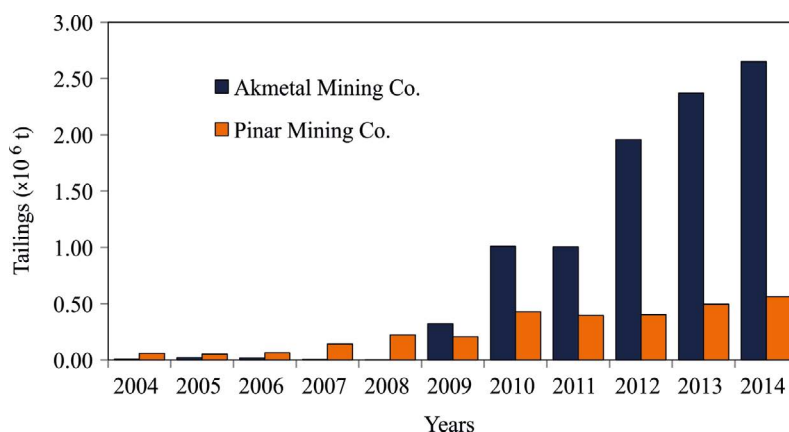


Fig. 1. Tailing quantities of the biggest 2 plants in the last 10 years

Rys. 1. Ilości odpadów w dwóch największych zakładach w okresie ostatnich 10 lat

Serpentine, rock which composes largely of serpentine minerals (include three minerals chrysotile, lizardite, and antigorite, all of which have similar compositions based on the presence of the main  $Mg_3Si_2O_5(OH)_4$  core, and differ slightly in the degree of substitution of Mg by Fe and Al), can be found in alpine-type settlings and as rocks dredged from the ocean bottom (El-leef et al. 2012). Serpentine is characterized by high levels of magnesium (ca. 35 wt% MgO), low calcium and aluminium content (ca. 1–4 wt% CaO and  $Al_2O_3$ ). This mineral can be utilized in numerous applications such as soil amelioration, extraction of amorphous silicate and pure magnesium compounds (Zengin et al. 2009; Fedorockova et al. 2012; Gao et al. 2014).

There are three magnesium production processes as known: silicothermal, carbothermal and electrolytic. In electrolytic route, magnesium metal is produced from magnesium-containing salts such as carnallite, bischofite, etc. by molten salt electrolysis method as seen at Equations (1) and (2):



The most important industrial magnesium production project by utilization of serpentine is Magnola Process by now. In the Magnola process, the leaching reaction generated soluble magnesium and an amorphous silica reaction product. The magnesium is converted from a silicate form into molten anhydrous magnesium chloride and then electrolyzed in a multipolar cell (Polmear 1999; Dutrizac et al. 2000; Watson et al. 2000). Synthetic amorphous silica has a wide range of usage area for industrial applications as filler in rubber and tires, whiteness agent and printability improver in paper and paint, etc. Also, materials containing high grade  $\text{SiO}_2$  can be utilized by photovoltaic industry which uses silicates to make solar panels (Khattak et al. 2001; Xakalashe and Tangstad 2011).

The most suitable treatment method to remove impurities from magnesium chloride solutions is fractional precipitation of hydroxides. Purified magnesium chloride solutions must be approximately neutral and the content of impurities in them must be no longer than ( $\text{g}/\text{dm}^3$ ): 0.26 Fe, 0.08 Si, 0.003 Ni, 0.004 Cu, 0.03 Mn, 0.013 Al, 0.009 Ti and 0.004 Cr (Strelets 1977; Gladikova et al. 2008).

In the present study; magnetic separation, leaching, precipitation and evaporation tests were consecutively performed. Mineral carnallite and amorphous silica were obtained. There are a lot of studies for recovering chromite from the tailings by magnetic separation in the literature (Guney et al. 2001; Aslan and Kaya 2009; Tripathy et al. 2013). But these studies only intend to recover chromite content. Present study is separated from the others by providing 3 products from the tailings: carnallite, amorphous silica and chromite.

## 1. Experimental

### 1.1. Materials

Chromite ore beneficiation plant tailings of Pinar and Akmetal companies located in Aladag district of Adana in Turkey were chosen as materials. In the plants, the tailings are divided into two fractions by sizes: coarse ( $d_{50}$ : 0.38 mm) and fine tailings ( $d_{50}$ : 0.18 mm). The fine tailings are about 60% of the total tailings. The fine tailings were used in the all experimental study.

As can be seen in Table 2, the loss on ignition rate is more than 15% and this confirms that the tailings are strongly serpentinized according to Bron et al. (1967). It was determined that the fine sized tailings consist of antigorite (serpentine), chromite, manganese oxide, talc and montmorillonite minerals by Rigaku Miniflex II X-Ray Diffractometer (Fig. 2).

Table 2. Chemical analysis of the fine sized tailings

Tabela 2. Analiza chemiczna odpadów drobnoziarnistych

Component	%
SiO <sub>2</sub>	38.55
MgO	30.55
Fe <sub>2</sub> O <sub>3</sub>	10.53
Cr <sub>2</sub> O <sub>3</sub>	3.44
Al <sub>2</sub> O <sub>3</sub>	0.77
MnO	0.47
CaO	0.44
NiO	0.07
Loss on ignition	15.18

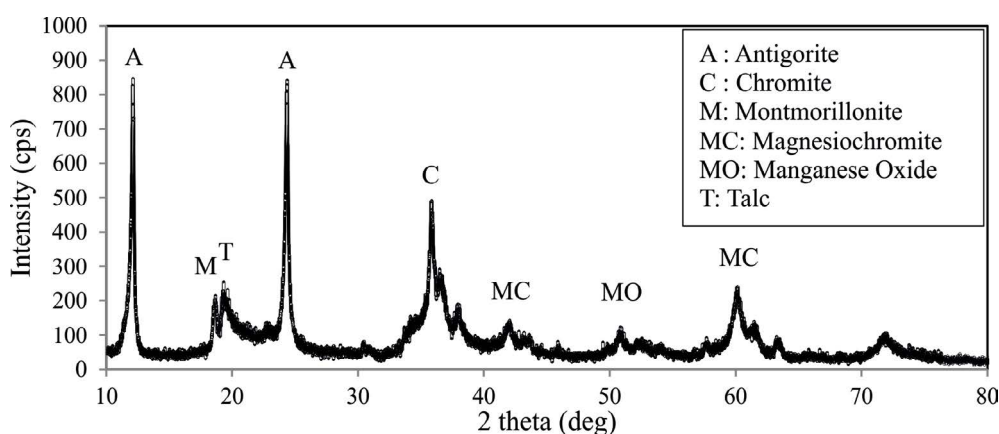


Fig. 2. XRD pattern of the fine sized tailings

Rys. 2. Dyfraktogram rentgenowski XRD drobnych kruszyw

Fine samples which chemical analysis is demonstrated in Table 2 were ground by using 10.8 kg of steel balls, 0.35 kg of the samples at 72% solid/liquid ratio and 5 min in the laboratory scale ball mill and then used in the present study. Metallic contamination resulted from the milling was not important because metallic impurities will have discarded from the products in the following magnetic separation and precipitation tests. Grain size distributions of three fractions are seen in Fig. 3.

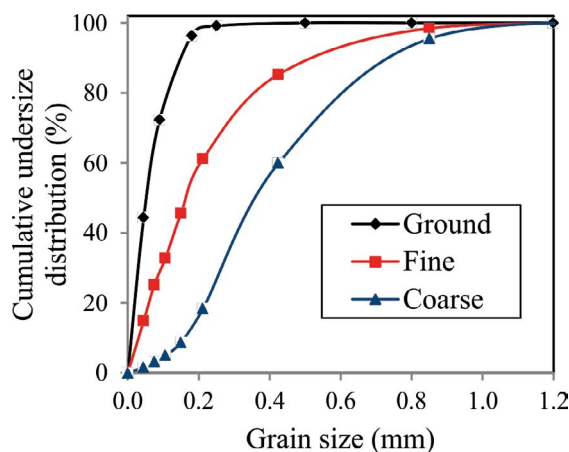


Fig. 3. Cumulative undersize distribution of the fine, coarse and ground tailings

Rys. 3. Skumulowana krzywa podsitowa ziarn drobnych, grubych i zmielonych odpadów

## 1.2. Methods

One-factor-at-a-time (OFAT) analysis was used to enlighten how the factors effect in the experiments. OFAT analysis consists of selecting a starting point, or baseline set of levels, for each factor, and then successively varying each factor over its range with the other factors held constant at the baseline level. After all tests are performed, a series of graphs are usually constructed showing how the response variable is affected by varying each factor with all other factors held constant.

In the tests, most of the magnetic minerals were discarded by using Eriez L4-20 WHIMS laboratory model high intensity wet magnetic separator at first. The pulp conditioned in a 500 cm<sup>3</sup> beaker being agitated by magnetic stirrer was fed into the magnetic separator. Magnetic separation products were dried and weighed. Non-magnetic phase was leached with HCl and amorphous silica was achieved by filtration as solid material. The reaction between HCl and the tailings was performed in a 250 cm<sup>3</sup> beaker equipped with a thermometer and a magnetic stirrer under atmospheric pressure. pH of the leach solution was raised by adding solid Mg(OH)<sub>2</sub> and the impurities were precipitated. After the filtration, the purified MgCl<sub>2</sub> solution was mixed with solid KOH pellets and the evaporation was begun to synthesize carnallite (Fig. 4).

Solid/liquid ratio, stirrer speed, stirring time and magnetic field strength were chosen as the varying parameters in the magnetic separation tests. Molarity of HCl, leaching time, stirrer speed, solid/liquid ratio and temperature were selected as the parameters to be optimized in the leaching tests. During the all tests, Fe and Mg contents were analysed with

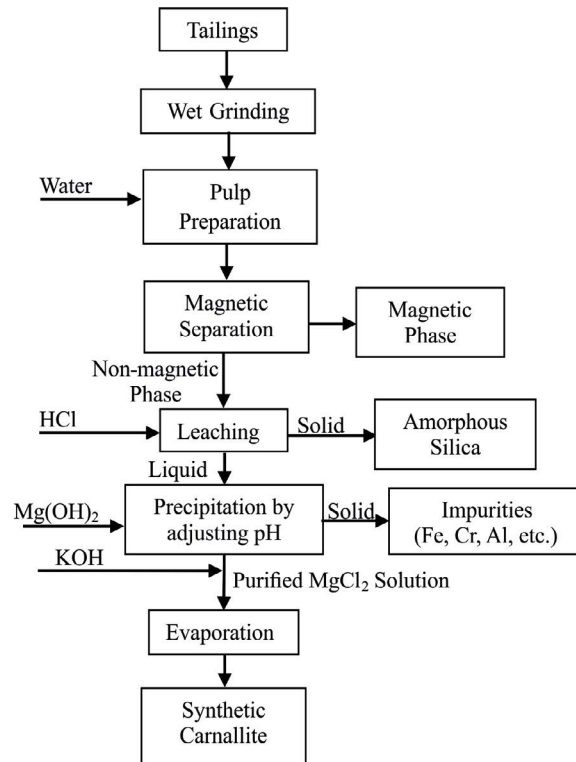


Fig. 4. Basic flow sheet of the experimental study

Rys. 4. Schemat badań otrzymywania karnalitu

EDTA drop titration method and the other elements were determined by Perkin Elmer PinAAcle 900 H atomic adsorption spectrophotometer (AAS). Analytic grade chemicals of Merck, Sigma Aldrich, Alfa Aesar with tap water in the Cukurova University laboratories were used throughout the study. Mg, Fe and the other impurities in the tap water were specifically excluded from the calculations. This method was chosen because it would not be easy to put that study into effect with economic reasons. Distilled water would not be used if beneficiation of these tailings would be performed in the industrial scale. Moreover, all of the impurities except calcium and magnesium ions in tap water will have precipitated by increasing the pH in the method applied by this study.

## 2. Results and Discussion

### 2.1. Magnetic Separation

It is known that chromite dissolve in HCl solutions almost never. Traditional chromite dissolution methods mostly depend on hydrofluoric (HF), perchloric ( $\text{HClO}_4$ ), phosphoric

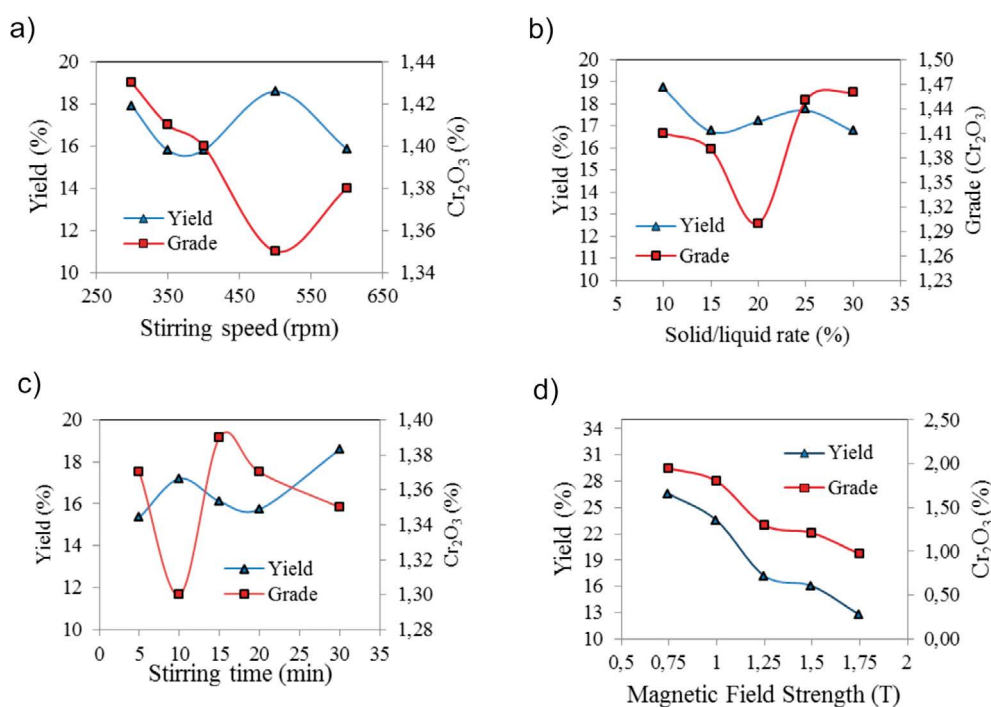


Fig. 5. a) Effect of the stirring speed on chromite yield and grade of the non-magnetic fraction (solid/liquid rate: 20%; stirring time: 10 min; magnetic field strength: 1.25 T),  
 b) Effect of the stirring time on chromite yield and grade of the non-magnetic fraction (solid/liquid rate: 20%; magnetic field strength: 1.25 T; stirring speed: 500 rpm),  
 c) Effect of the solid rate on chromite yield and grade of the non-magnetic fraction (solid/liquid rate: 20%; stirring time: 10 min; magnetic field strength: 1.25 T),  
 d) Effect of magnetic field strength on chromite yield and grade of the non-magnetic fraction (solid/liquid rate: 20%; stirring time: 10 min; stirrer speed: 500 rpm).

Rys. 5. a) Wpływ szybkości mieszania na wydajność i stopień chromitacji frakcji niemagnetycznej (stosunek ciało stałe/ciecz: 20%, czas mieszania: 10 minut, natężenie pola magnetycznego: 1,25 T);  
 b) wpływ czasu mieszania na wydajność i stopień chromitacji frakcji niemagnetycznej (stosunek ciało stałe/ciecz: 20%, natężenie pola magnetycznego: 1,25 T, szybkość mieszania: 500 obr./min);  
 c) wpływ stosunku ciała stałego na wydajność chromitu i stopień chromitacji frakcji niemagnetycznej (stosunek ciało stałe/ciecz: 20%, czas mieszania: 10 min, natężenie pola magnetycznego: 1,25 T);  
 d) wpływ pola magnetycznego na wydajność i stopień chromitacji frakcji niemagnetycznej (stosunek ciało stałe/ciecz: 20%, czas mieszania: 10 minut, szybkość mieszadła: 500 obr./min)

( $\text{H}_3\text{PO}_4$ ) and sulphuric ( $\text{H}_2\text{SO}_4$ ) acids in addition to alkali leaching (Geveci et al. 2002; Chen et al. 2014; Spectroscopyonline.com 2014). Therefore, main purpose of the magnetic separation was particularly to eliminate the chromite content in addition to the iron and manganese contents before the leaching. Chromite yield and grade of the non-magnetic fraction were taken into consideration since non-magnetic fraction will be used in the following leaching stage.

Effects of the stirrer speed, stirring time, solid/liquid ratio and magnetic field strength on the magnetic separation were investigated in succession. The best result for stirring speed tests was obtained at 500 rpm which chromite grade of the non-magnetic phase was minimum (Fig. 5a). In the stirring time tests, 10 min stirring time was determined as convenient time (Fig. 5b). The best result in the solid/liquid ratio determining stage was 20% which chromite grade of the non-magnetic phase was the lowest (Fig 5c). The chromite grade and yield of the non-magnetic material decreased as the magnetic field strength increased (Fig. 5d). It was found that the stirrer speed and the magnetic field strength were effective parameters on magnetic separation rather than the others.

Optimum conditions for the magnetic separation were found as 500 rpm stirrer speed, 20% solid/liquid ratio, 10 min stirring time and 1.75 T magnetic field strength. Chemical analysis of the non-magnetic material acquired from the above mentioned conditions is seen in Table 3. The results indicated that 85.75% of  $\text{Cr}_2\text{O}_3$ , 91.22% of MnO and 64.71% of  $\text{Fe}_2\text{O}_3$  were removed. Iron removal was low in the magnetic separation in comparison to the other magnetic contents because the iron content, which can be found in the mineral antigorite ( $(\text{Mg,Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$ ) as the element Fe, could not be separated by the magnetic separation that is a physical method. Obtained non-magnetic material was 51.61% of the original sample by weight. It was dried and collected for using in the next leaching stage. Also,

Table 3. Chemical analysis of the non-magnetic material

Tabela 3. Analiza chemiczna materiału niemagnetycznego

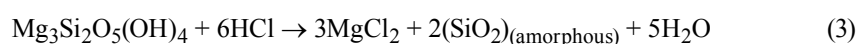
Component	%
$\text{SiO}_2$	40.04
MgO	33.83
$\text{Fe}_2\text{O}_3$	7.20
$\text{Cr}_2\text{O}_3$	0.95
$\text{Al}_2\text{O}_3$	0.72
MnO	0.08
CaO	0.94
NiO	0.05
Loss on ignition	16.19



the magnetic material was recovered with 6.10% Cr<sub>2</sub>O<sub>3</sub> grade and 85.75% Cr<sub>2</sub>O<sub>3</sub> recovery yield. It is thought that Cr<sub>2</sub>O<sub>3</sub> cannot be separated completely by any physical beneficiation method even if particle sizes are reduced. Chromium in the samples is not only in the chromite ore form which has FeCr<sub>2</sub>O<sub>4</sub> formula but also in the magnesiochromite forms presented by MgCr<sub>2</sub>O<sub>4</sub> or MgFeCr<sub>2</sub>O<sub>4</sub> formulas.

## 2.2. Leaching

The main leaching reaction is shown in Equation (3):



The dissolutions of Mg, Fe, Ca, Mn, Cr and Ni in HCl solutions were studied. Non-magnetic material was leached at different acid molarities, temperatures, solid/liquid ratios, stirrer speeds and time intervals, respectively. As seen in Fig. 6a, extraction of the elements was mostly increased in direct proportion to HCl concentration, but dissolved Mg<sup>2+</sup> ions were steady over the 7 M of HCl solution while Ca<sup>2+</sup> ions were completely dissolved for the each M of HCl. The experiments plotted in Fig. 6b revealed that the stirrer speed was not significant in the leaching between the speeds 150–550 rpm. The extraction rates were found to be dependent on the temperature, especially over 60°C (Fig. 6c). In spite of the high temperatures, chromium still did not passed into the leach solution. All the contents were extracted from the solid sample at 90°C almost completely except chromium and silica. From Fig. 6d, it can be said that leaching of the sample was substantially completed at the first 30 min. Then, extraction rates slightly increased. As shown in Fig. 6e, dissolution rates were decreased as the solid/liquid ratios were increased. The rates of the Mg<sup>2+</sup> ions had dramatic drop over 11%, surprisingly. The optimal conditions were revealed as following: stirrer speed: 300 rpm; stirring time: 30 min; temperature: 90°C; HCl concentration: 7 M, solid/liquid ratio: 11% (Table 4).

Table 4. Content of the leach solution at optimum conditions

Tabela 4. Zawartość roztworu ługującego w warunkach optymalnych

Element	Mg	Fe	Cr	Mn	Ca	Ni
mg/L	6 744.00	1 470.00	4.12	11.60	243.72	12.20

The extraction rates were found to be dependent on temperature and HCl concentration rather than leaching time and solid/liquid rate. There was no correlation between the stirrer speed and the leaching.

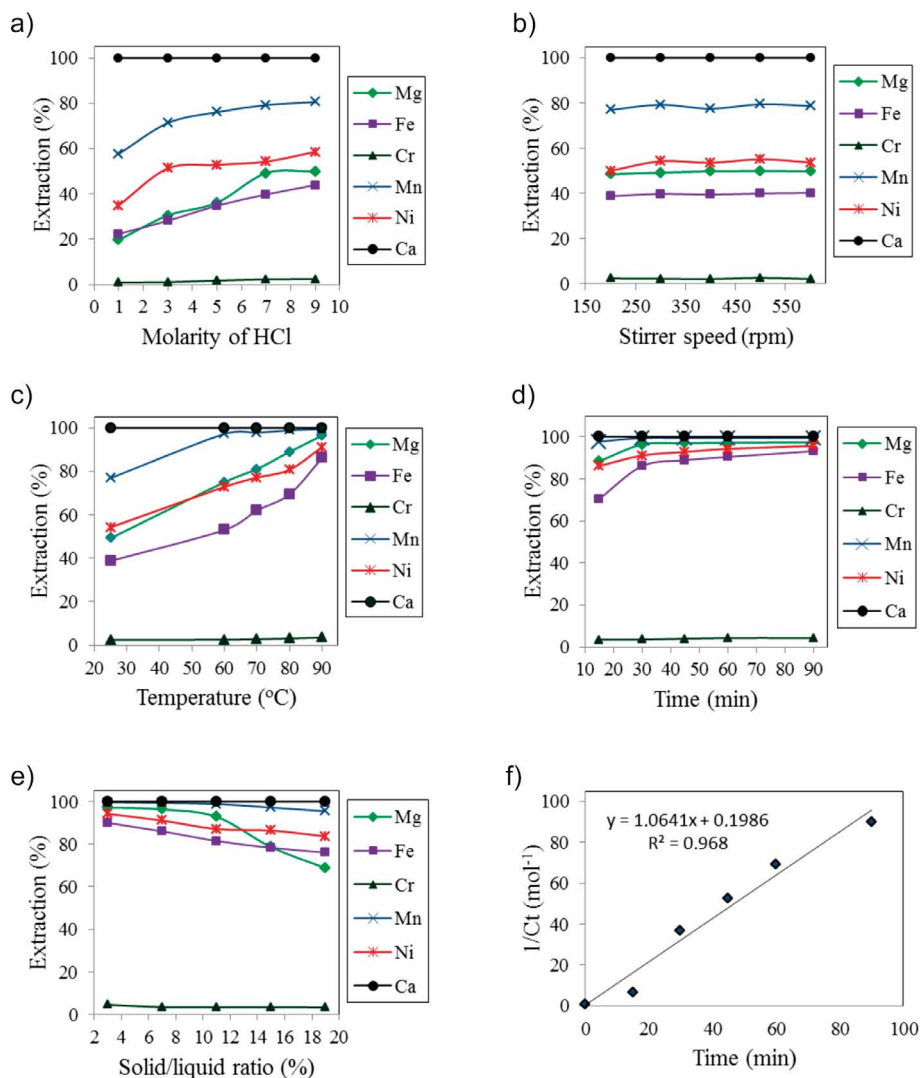


Fig. 6. a) Effects of HCl concentration (solid/liquid rate: 7%; stirring time: 30 min; stirrer speed: 300 rpm, temperature: 25°C), b) stirrer speed (solid/liquid rate: 7%; stirring time: 30 min; HCl concentration: 7 M, temperature: 25°C), c) temperature (solid/liquid rate: 7%; stirring time: 30 min; stirrer speed: 300 rpm; HCl concentration: 7 M), d) time (solid/liquid rate: 7%; stirrer speed: 300 rpm; temperature: 90°C; HCl concentration: 7 M), e) solid/liquid rate (stirrer speed: 300 rpm; stirring time: 30 min; temperature: 90°C; HCl concentration: 7 M) on leaching and f) the second order dissolution kinetics of magnesium

Rys. 6. a) Wpływ stężenia HCl (stosunek ciało stałe/ciecz: 7%, czas mieszania: 30 minut, szybkość mieszadła: 300 obr./min, temperatura: 25°C); b) szybkość mieszania (stosunek ciało stałe/ciecz: 7%, czas mieszania: 30 min, stężenie HCl: 7 M, temperatura: 25°C); c) temperatura (ciało stałe/ciecz: 7%, czas mieszania: 30 min, szybkość mieszadła: 300 obr./min, stężenie HCl: 7 M); d) czas (stosunek ciało stałe/ciecz: 7%, szybkość mieszadła: 300 obr./min, temperatura: 90°C, stężenie HCl: 7 M), e) stała prędkość mieszania: 300 obr./min, czas mieszania: 30 minut, temperatura: 90°C, Stężenie HCl: 7 M) na ługowanie; f) kinetykę rozpuszczania magnezu drugiego rzędu

The magnesium dissolution from serpentine in HCl solutions was described in the form of Equation (4) by Teir et al. (2007):

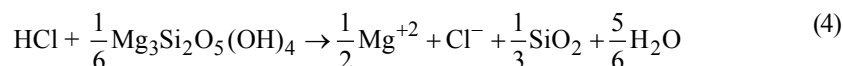


Fig. 6f was created by using molar dissolution rates of magnesium in Fig 6d which temperature of the leaching was constant. The reaction of the leaching process was found to be pseudo second order. Rate constant ( $k$ ) of this reaction was determined as 1.0641 which is the slope of linear line in Fig 6f. It was detected that Equation (5) can be written to explain magnesium dissolution from these type tailings:

$$\frac{1}{c_t} = kt + \frac{1}{c_o} \quad (5)$$

- ✚  $C_t$  – equilibrium concentration [ $\text{mg}/\text{dm}^3$ ],
- $C_o$  – initial concentration [ $\text{mg}/\text{dm}^3$ ],
- $t$  – time [min],
- $k$  – rate constant [ $\text{dm}^3/\text{mg}\cdot\text{min}$ ].

Magnesium dissolution rates have the highest correlation with nickel ( $R^2 = 0.98$ ) and iron ( $R^2 = 0.91$ ) dissolution values (Fig. 7). Manganese, which is one of the easiest soluble material in HCl, and chromium, which is one of the hardest soluble material in HCl, dissolution values ( $R^2 = 0.87$  and  $0.72$ , respectively) show the lower correlation with magnesium

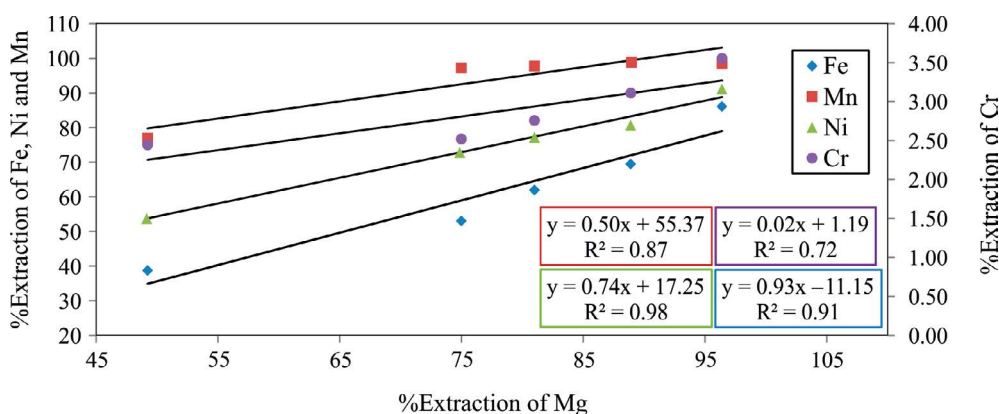


Fig. 7. Extraction correlation for magnesium, iron, chromium and nickel in the HCl leaching (Extraction values were taken from Fig. 6c)

Rys. 7. Korelacja ekstrakcji magnezu, żelaza, chromu i niklu w ługowaniu HCl (wartości ekstrakcyjne pobrano z rys. 6c)

dissolution values by comparison with the Ni and Fe dissolutions. It can be deduced that the selective extraction of metals from these solid samples except for chromium is not possible by leaching. The metals can be obtained from the leach solution by solvent extraction, selective precipitation or the other methods after the solid/liquid separation.

The solid residue generated after leaching was in the form of amorphous silica which is known for characteristic diffused broad peak at 2 theta: 22.141 (Fig. 8; Table 5) (Javed et al. 2010). Basically, insoluble contents in this residue were chromite and antigorite minerals.

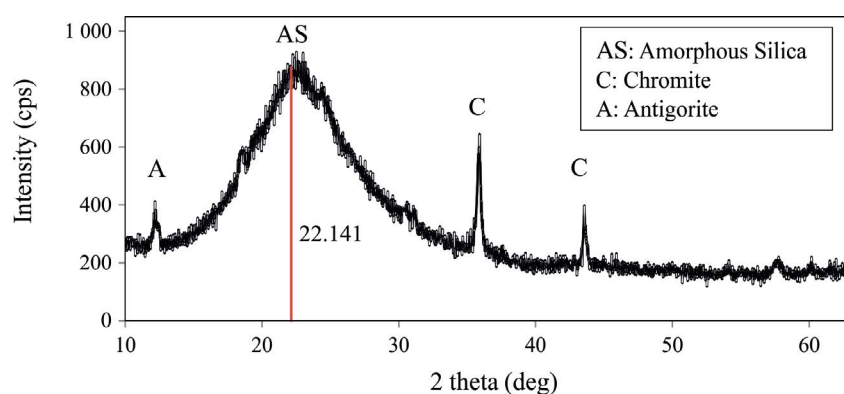


Fig. 8. XRD Pattern of the leach residual

Rys. 8. Dyfraktogram rentgenowski XRD pozostałości po ługowaniu

Table 5. Composition of the leach residual at optimum conditions

Tabela 5. Skład pozostałości ługu w warunkach optymalnych

Component	SiO <sub>2</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	NiO	MnO
%	86.28	6.14	3.39	2.35	1.81	0.01	0.02

### 2.3. Magnetic Separation Tests Following the Leaching

High intensity wet magnetic separation was carried out at the previous optimum magnetic separation conditions again in order to remove metallic impurities from the leach residuals (Fig. 9). Amorphous silica grade was raised to 96.5% SiO<sub>2</sub> with 84.38% total recovery yield after consecutive two magnetic separations (Table 6).

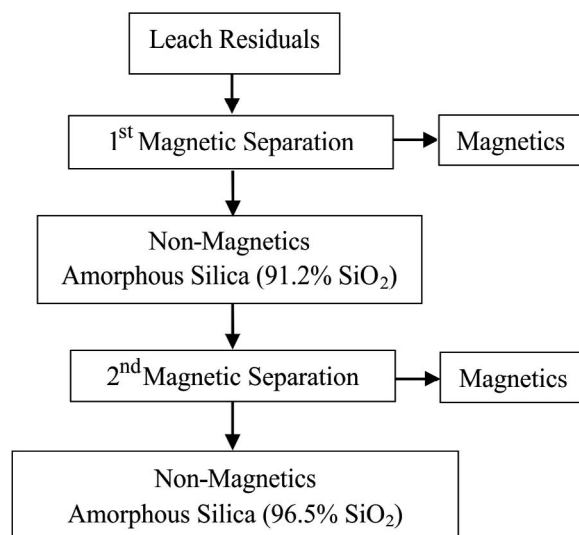


Fig. 9. Flow chart of the additional magnetic separations

Rys. 9. Schemat blokowy dodatkowych separacji magnetycznych

Table 6. Composition of the non-magnetic material after the separation twice

Tabela 6. Skład materiału niemagnetycznego po dwukrotnej separacji

Component	SiO <sub>2</sub>	MgO	Cr <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>
%	96.50	1.19	1.07	1.00	0.24

## 2.4. Precipitation

Magnesium hydroxide was fed into a predetermined volume of the leach solution in order to remove the impurities and the solution pH was raised by this route. When Mg(OH)<sub>2</sub> was added to the leach solution, not only concentration of magnesium ions increased but also impurities except calcium ions, which generally precipitate with magnesium ions above pH 10, precipitated as their hydroxide forms. Different pH values were chosen to specify an optimal pH value (Fig. 10, 11). The contents of the leach solution obtained after solid/liquid separation is seen in Table 7. Solid MgO could have used instead of Mg(OH)<sub>2</sub> by providing the same effect. NH<sub>3</sub> or NaOH could be selected for upgrading the pH, but contamination possibility of magnesium chloride solution with impurities such as Na and N eliminated these options.

Table 7. Contents of the purified magnesium chloride solution at pH 8

Tabela 7. Zawartość oczyszczonego roztworu chlorku magnezu w pH 8

Element	Mg	Fe	Cr	Mn	Ni	Ca
mg/L	12 040	–	–	4.42	0.09	280

As a result of the precipitation tests, the solution obtained from solid/liquid separation at pH 8 was used in the following crystallization tests.

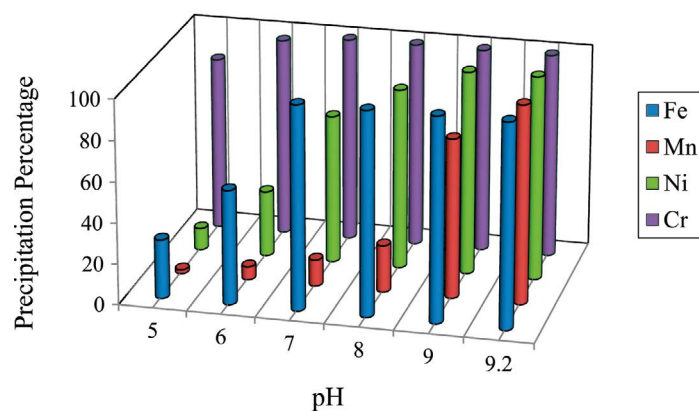


Fig. 10. Precipitation percentage of the impurities by pH

Rys. 10. Udział procentowy osadów zanieczyszczeń w zależności od pH

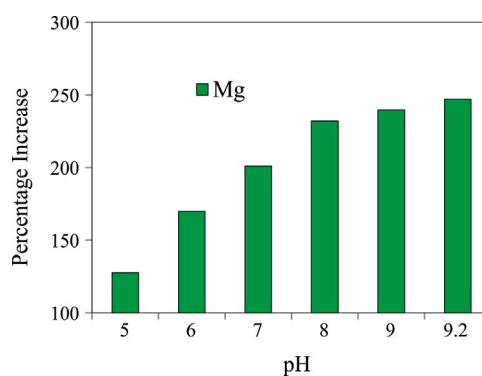


Fig. 11. Percentage increase of the magnesium content by pH

Rys. 11. Procentowy wzrost zawartości magnezu w zależności od pH

## 2.5. Crystallization

The purified magnesium chloride solution taken from previous pH increasing stage was mixed with solid KOH pellets at 90°C, stoichiometrically. After obtaining the clear and colourless solution, the final solution was evaporated between 90–10°C by controlled heating. Finally, white residual was obtained and ground in order to analyse.

It was observed that XRD peaks of the synthesized material in Fig. 12 matched with the carnallite mineral (Mineralienatlas.de 2014; Mindat.org 2014). Also, chemical analysis of this material confirmed that the mineral carnallite was synthesized (Table 8).

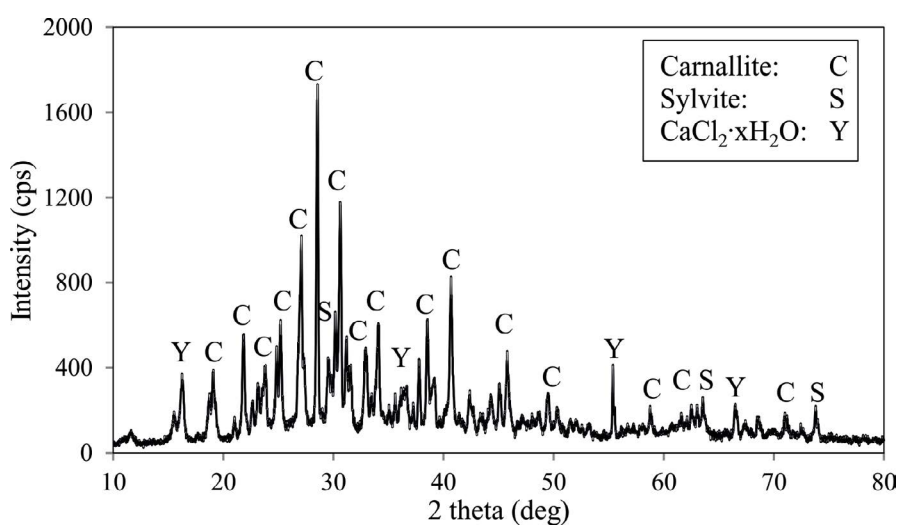


Fig. 12. XRD pattern of the synthesized carnallite

Rys. 12. Dyfraktogram rentgenowski XRD syntetycznego karnalitu

Table 8. Chemical analysis of the synthesized carnallite

Tabela 8. Analiza chemiczna syntetyzowanego karnalitu

Compound	%
MgO	17.40
Cl	34.60
K <sub>2</sub> O	21.40
CaO	0.87
MnO	0.04
H <sub>2</sub> O	25.69

## Conclusions

Present study indicates that synthetic carnallite can be prepared from chromite ore beneficiation plant tailings by extracting and purifying the magnesium content in these tailings. Besides, high grade amorphous silica ( $\text{SiO}_2 > 96\%$ ), which is suitable raw material for the production of photovoltaic solar panels because of not containing boron and phosphorus, can be obtained by HCl leaching as leach residual. For these purposes, optimum magnetic separation, leaching and precipitation parameters were determined.

Chromite cut-off grade plummeted to 4–5%  $\text{Cr}_2\text{O}_3$  in Aladag district. In this context, it can be said that the magnetic material, which is obtained from the first single stage magnetic separation with 6.10%  $\text{Cr}_2\text{O}_3$  grade and 85.75%  $\text{Cr}_2\text{O}_3$  recovery yield, can be fed to the concentration plants in order to upgrade the  $\text{Cr}_2\text{O}_3$  grade to saleable  $\text{Cr}_2\text{O}_3$  grade ( $\text{Cr}_2\text{O}_3 > 46\%$ ).

It is thought that required additional  $\text{Mg}(\text{OH})_2$  amount and HCl concentration in the leaching stage can be reduced by high pressure leaching. Also, high intensity dry magnetic separation can be used for removal of the magnetic particles in the amorphous silica product in order to upgrade the  $\text{SiO}_2$  content. Studies about these options are planned for the further researches.

### Acknowledgement

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**WYTWARZANIE SYNTETYCZNEGO KARNALITU I AMORFICZNEJ KRZEMIONKI  
Z ODPADÓW WZBOGACANIA RUD CHROMITOWYCH**

## Słowa kluczowe

syntetyczny karnalit, bezpostaciowa krzemionka, wzbogacanie magnetyczne, odzysk

## Streszczenie

W artykule przedstawiono badania możliwości wytwarzania karnalitu ( $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ ) i bezpostaciowej krzemionki ( $\text{SiO}_2$ ) z odpadów z zakładów procesu wzbogacania chromitów, które zawierają 3,44% wag. chromitu ( $\text{Cr}_2\text{O}_3$ ) i 30,55% wag. tlenku magnezu ( $\text{MgO}$ ). W skali laboratoryjnej do usuwania materiałów magnetycznych, takich jak: chromit, żelazo (II) i minerały manganowe (II) zastosowano wzbogacanie mokre w separatorach magnetycznych o wysokiej intensywności. Około 85,75% chromitu, 91,22% MnO i 64,71%  $\text{Fe}_2\text{O}_3$  usunięto metodą jednoetapowej separacji magnetycznej. Po wzbogacaniu magnetycznym odzysk hydrometalurgiczny został zainicjowany przez ługowanie odpadów kwasem chlorowodorowym (HCl). Amorficzne cząstki krzemionki i inne substancje stałe oddzielono od roztworu ługującego przez filtrację. Z roztworu ługowanego wytrąciły się zanieczyszczenia przez wzrost pH dzięki zawartemu wodorotlenkowi magnezu ( $\text{Mg}(\text{OH})_2$ ). Oczyszczony roztwór chlorku magnezu ( $\text{MgCl}_2$ ) zmieszano z wodorotlenkiem potasu (KOH) w stosunku stechiometrycznym. Zgodnie z XRD i analizą chemiczną, syntetyczny karnalit syntetyzowano przez kontrolowane ogrzewanie tego roztworu w temperaturze 90–100°C. Również odzysk 84,38% amorficznej krzemionki o zawartości 96,5%  $\text{SiO}_2$  uzyskano przez dodatkowe magnetyczne wzbogacanie.

**PREPARATION OF SYNTHETIC CARNALLITE AND AMORPHOUS SILICA FROM  
CHROMITE BENEFICIATION PLANT TAILINGS**

## Keywords

synthetic carnallite; amorphous silica; mineral processing; recovery.

## Abstract

In this paper, synthetic carnallite ( $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ ) and amorphous silica ( $\text{SiO}_2$ ) preparation possibilities were investigated by utilizing chromite beneficiation plant tailings which contain 3.44% chromite ( $\text{Cr}_2\text{O}_3$ ) and 30.55% magnesium oxide ( $\text{MgO}$ ) by weight. Firstly, laboratory scale high intensity wet magnetic separator was applied for removing the magnetic materials such as chromite, iron (II) and manganese (II) minerals in the tailings. About 85.75% of chromite, 91.22% of MnO and 64.71% of  $\text{Fe}_2\text{O}_3$  were removed by single stage magnetic separation. After the magnetic separation, hydrometallurgical recovery was initiated by leaching of the tailings with hydrochloric acid (HCl). Amorphous silica particles and the other solids were separated from the leach solution by filtration. Impurities were precipitated from the leach solution by elevating the solution pH via magnesium

hydroxide ( $\text{Mg}(\text{OH})_2$ ) adding. The purified magnesium chloride ( $\text{MgCl}_2$ ) solution was mixed with potassium hydroxide (KOH) at stoichiometric ratio. According to the XRD and chemical analysis, the synthetic carnallite was synthesized by controlled heating of this solution at 90–100°C. Also, the amorphous silica with 96.5%  $\text{SiO}_2$  content and 84.38% recovery yield was obtained by additional magnetic separation treatment.

