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# COMPARATIVE STUDY OF PROPERTIES OF CHROMITE SINTERING PRODUCTS

The aim of the work was to compare the properties of chromite sintering products derived from the industrial process of sodium chromate winning. The investigations were carried out on two kinds of products. The first sample was obtained in a modified process of sodium chromate production relying on sintering chromite ore with soda, calcium oxide, and chromium waste. The second sample was derived from the dolomitic process which is commonly used in industrial practice.

The phase (microscope observations, X-ray diffraction, infrared spectrophotometry) and chemical analyses were applied. In accordance with the assumption, the main component of the obtained sinter was sodium chromate being a soluble phase. The content of this compound was from 0.175 to 0.236 kg $CrO_3$/kg of charge. The constituents of the insoluble fraction of tested sinters were periclase (MgO), calcium oxychromite ($9CaO \cdot 4CrO_3 \cdot Cr_2O_3$), chromopicotite ($((Fe,Mg)(Cr,Al,Fe)_2O_4$ and dicalcium silicate ($2CaO \cdot SiO_2$).

It was found that both materials have similar phase composition but different contribution of the above mineral phases. The sinters derived from the dolomite process contained additionally brownmilleritte. The tested sinters differ in softening points. Other physicochemical properties of the sinters derived from the modified process of sodium chromate production are similar with the ones for the sinters derived from the dolomite method.

*Keywords: sodium chromate(VI), modified process, chromium compounds winning*

## INTRODUCTION

Sodium chromate is the main intermediate product used in manufacturing of all other chromium compounds. The winning of this compound from chromite ores or its concentrates has been traditionally achieved by a roasting process of mixture containing ore, soda-ash and diluent. The kind and amount of diluent influence essentially the working load of the blend rotary kiln as well as the amount of chromium waste material (so called chromic mud) in the blend. An improper choice of the blend leads to the formation of accretions in the hot part of the rotary kiln, which is

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a result of lowering of the softening and melting points of sinter. This influences the efficiency of the chromate extraction. The residue – chromic mud generated during this process is commonly dumped at special heaps. This mud contains hexavalent chromium Cr(VI) and for this reason the residue has become a major problem from the industry connected with the chromium compounds production. The technological aspects of utilization of chromic mud were presented for example by Jarosiński and Maczka, 2001 as well as Kowalski and Wzorek, 2002.

Until 1999 sodium chromate was produced with the use of the classic dolomite method, which generated large amounts of the chromic mud. This year in Poland a modified process was implemented based on substitution of the chromite ores by a chromic waste derived from the chromium compounds winning. In the process of sodium chromate production such materials as e.g. chromic mud, waste consisting of hydrated chromium oxides and various kinds of recycling (in-process and off-process) materials (Kowalski, 2002; Kowalski and Walawska, 2002) are applied. The modified method is more efficient in material and energy consumption in relation to the dolomite process. Moreover, the amount of generated residue in the modified process is significantly lower than that in the dolomite process.

A comparative study of properties of sinters derived from the dolomite and the modified processes of sodium chromate production is conducted in this paper. The obtained results should contribute to our understanding of the dependence of the physicochemical properties of the sinter on its structure.

## EXPERIMENTAL

The following materials were used for the studies. Sinter derived from the dolomite process and sinters obtained by the modified process of sodium chromate winning. 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. The diffraction patterns were obtained employing a Philips diffractometer. The spectrophotometrical analysis in the infrared region was carried out with the use of a DIGITAL AB Scimitar Series apparatus with the application of pressed pellets containing KBr and the sample.

Microscopic examination of the tested sinters was carried out using an optical microscope and scanning electron microscope "JEOL". The sintering and softening points of the investigated samples were determined using a hot-stage microscope (Leitz). The observations of samples in the range 20 - 1500$^{o}$C in an oxidizing atmosphere were conducted.

## RESULTS AND DISCUSSION

The chemical analysis of the investigated samples is presented in Table 1. As can seen in Table 1, the amount of soda-ash in charges was for all mixtures lower than the stoichiometric quantity of this compound needed to association of chromium with sodium chromate. In the case of sinter 3, the molar ratio $M_{Na}$ was higher in relation to the other sinters. According to the technological assumptions, the quantity of lime was enough to chemically bind silica by dicalcium silicate. Particularly, a large excess of lime was in sinter 3.

Table 1. The chemical composition of the investigated sinters [%]

| Component | Sinters* | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| $CrO_3$ | 24.4 | 22.6 | 25.1 |
| $Cr_2O_3$ | 2.16 | 1.7 | 5.1 |
| $Al_2O_3$ | 9.4 | 4.8 | 4.8 |
| $Fe_2O_3$ | 9.7 | 5.5 | 5.5 |
| CaO | 15.8 | 18.0 | 19.9 |
| MgO | 22.0 | 19.3 | 23.6 |
| $SiO_2$ | 7.0 | 6.6 | 4.4 |
| $Na_2O$ | 12.9 | 11.4 | 17.5 |
| Molar ratio: | | | |
| $M_{Na}$ [$Na_2O/CrO_3$] | 0.76 | 0.74 | 0.89 |
| $M_{CaO}$ {$CaO/SiO_2$] | 2.42 | 2.92 | 4.84 |

*1,2 – sinters obtained by the modified process - simples taken at one month intervals from the plant sodium chromate production, 3 – sinter derived from the dolomite process

The physicochemical properties of the tested samples are given in Table 2. It should be pointed out that degree of chromium oxidation for sinter obtained in the new process is higher than that for sinters derived from the dolomite process. Moreover, softening point for all tested samples amounted to ≥ 1200°C . The results indicate that under industrial conditions melted sinters and buildups practically did not form because the maximal temperature in the rotary kiln used in the process of sodium chromate winning amounted to 1150-1200°C. The sinters from the modified process feature a higher sintering point than sinters obtained by the dolomite process. These parameters influence the degree of chromium oxidation. The obtained productivity are comparably with the values presented by Kowalski et al., 2002.

On the basis of microscopic studies, it has been found that the mean particle diameter was 0,005 mm. In all tested samples the presence of fine crystalline irregular crystals forming numerous aggregates was observed. These aggregates are connected with a micro or fine crystalline structure or independent phase (Fig.1). The surface of grains was well developed. Part of particles had shape closed to spherical. The size of some sinters components is in the range of 0.005-0.04 mm in size.

An example of a microscopic image of thin shallows of the sinter is presented in Fig. 2. In all cases, fine microcrystalline and partly isotropic background with yellow colouring derived from sodium chromate was observed.

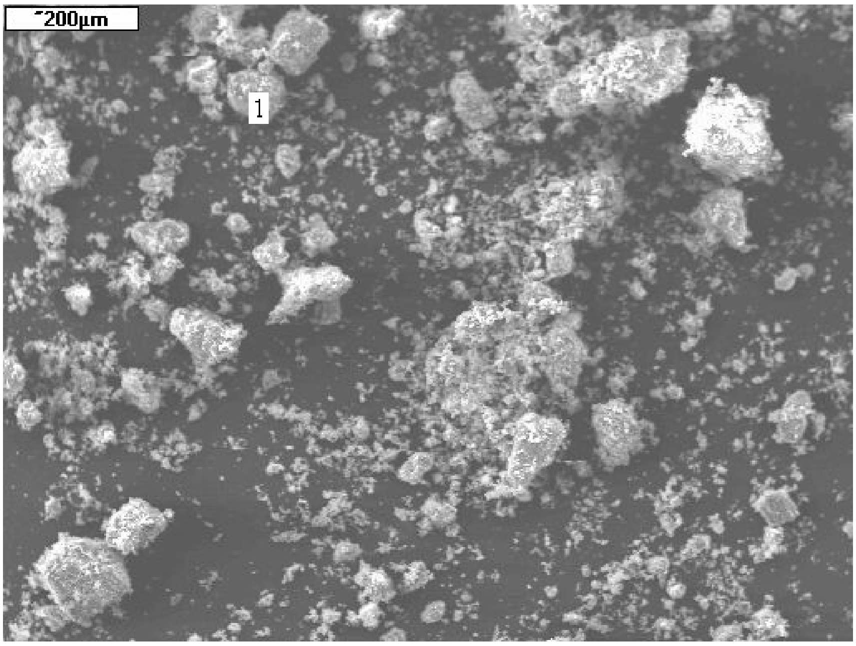


Fig.1. SEM micrograph of the tested sinter (sample 1)

Table 2. The physicochemical properties of investigated sinters

| Property | Dimension | Kind of sinter* | | |
|---|---|---|---|---|
| | | 1 | 2 | 3 |
| Specific gravity | kg $m^{-3}$ | 2950 | 3000 | 2990 |
| Degree of Cr oxidation | % | 89,7 | 91,1 | 78,9 |
| Productivity | kg $CrO_3$/kg of charge | 0.214 | 0.236 | 0.175 |
| Sintering point | $^{o}$ C | 1100 | 950 | 900 |
| Softening point | $^{o}$ C | 1280 | 1250 | 1200 |

*1,2 – sinters obtained in the modified process - simples taken at one month intervals from the plant sodium chromate production, 3 – sinter derived from the dolomite process

Moreover, the chromium minerals associated with calcium and iron phases were calcium oxychromite and chromopicotite. Especially, the later chromium phase appeared in small quantities. Among other minerals, the presence of colouress, turning into gray, isotropic periclase of high refractive index was observed. The sinter derived from the dolomite process contained also brownmillerite. Brownmillerite was not found in samples 1 and 2. The other iron phase in the above two sinters was hematite.

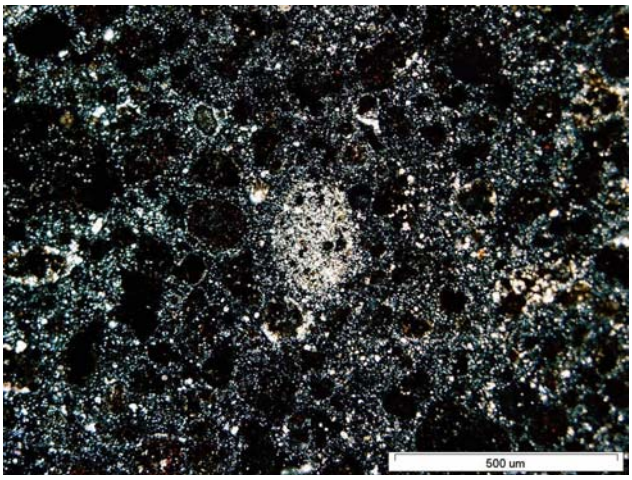


Fig. 2. Image of sinter after leaching of sodium chromate (sample 3)

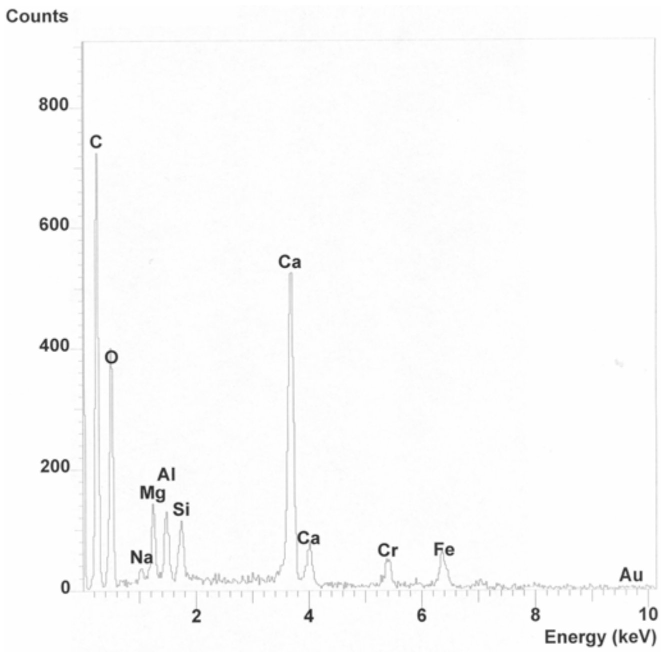


Fig.3. Results of EDS analysis (sample 1 – grain area No. 1)

Table 3. Results of X-ray analysis of tested sinters

| Kind of sinter | | | | Mineral phase |
|---|---|---|---|---|
| 1 | | 3 | | |
| d(nm) | I | d(nm) | I | |
| | | 7.34 | 20 | B. |
| 4.96 | 20 | 4.96 | 20 | S.C. |
| 4.05 | 65 | 4.06 | 65 | S.C. |
| 3.90 | 100 | 3.90 | 100 | S.C. |
| | | 3.67 | 30 | B. |
| 3.57 | 40 | 3.57 | 40 | S.C. |
| 2.90 | 100 | 2.90 | 100 | S.C., C.S., CP. |
| | | 2.78 | 30 | S.C., C.S., |
| 2.73 | 70 | 2.73 | 70 | S.C.,C.S. |
| | | 2.66 | 60 | B. |
| 2.615 | 85 | | | C.S. |
| 2.510 | 96 | | | H. |
| | | 2.466 | 30 | S.C. |
| | | 2.44 | 20 | B.,P. |
| 2.170 | 13 | | | S.C.,C.S. |
| | | 2.106 | 100 | P., C.S.,CP. |
| 2.100 | 100 | | | P.,CP., H., C.S. |
| 1.983 | 24 | | | C.S. |
| 1.941 | 60 | | | P.,H. |
| 1.780 | 20 | | | S.C. |
| 1.490 | 90 | | | P. |

S.C.-sodium chromate, C.S. – dicalcium silicate, B – brownmillerite, CP- chromopicotite, P- periclase, H- hematite

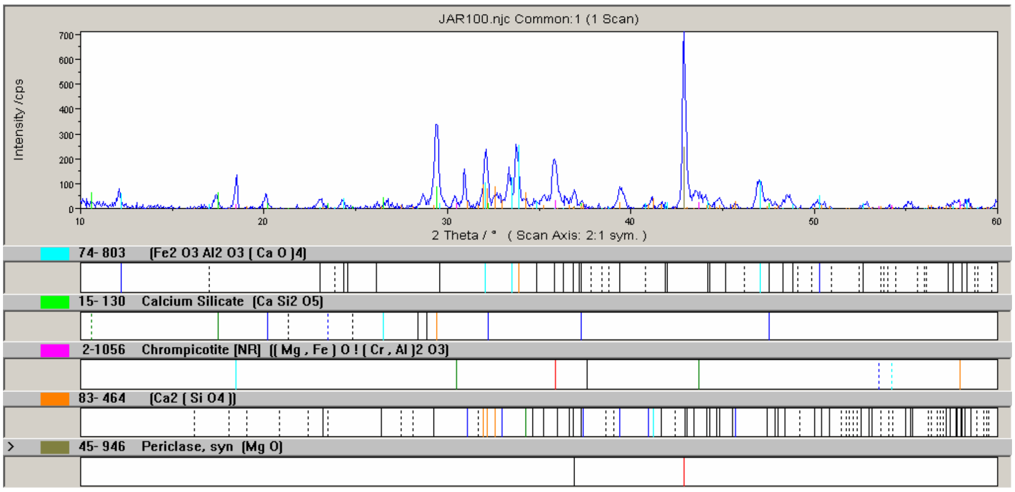


Fig. 4. X-ray diffraction pattern of sinter after leaching sodium chromate (sample 1)

Results of EDS analysis are presented in Fig. 3. The X-ray analysis confirmed the presence of the discussed minerals in the tested samples (Table 3 and Fig. 4.). The spectrophotometric analysis of the soluble phase showed a clear absorption band coming from chromates (850-950 $cm^{-1}$).

## CONCLUSION

The obtained results make it possible to determine quantitatively individual forms of chromium during the process. This is important for practical purposes. The carried out investigations proved that the degree of chromium oxidation was higher for charge containing chromium waste than for the blend prepared with dolomite diluent. According to a technological assumption, sodium chromate was a dominant mineralogical phase. Moreover, chromium is also present in the form of calcium oxychromite in all tested sinters. Chromopicotite occurred there as traces. In the insoluble fraction, the main phase was periclase. Moreover, dicalcium silicate was part of the phase composition of this fraction. Hematite was identified in sinters derived from the modified process. The presence of this phase in the sinter derived from the dolomite process was observed. The physicochemical properties of both investigated materials were similar, except the softening and sintering points.

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Celem pracy było porównanie właściwości fizykochemicznych produktów spiekania chromitów otrzymanych w procesie wytwarzania chromianu sodu w warunkach przemysłowych. Badania prowadzono dla dwóch rodzajów produktów. Pierwszy otrzymano w zmodyfikowanym procesie wytwarzania chromianu sodu, w którym wsad stanowiły takie składniki jak chromit, soda, tlenek wapnia oraz odpady tzw. błoto pochromowe. Drugi rodzaj spieku został pobrany z procesu wytwarzania tego związku metodą powszechnie stosowaną w praktyce przemysłowej – metoda dolomitowa. Ocenę składu mineralnego badanych próbek oparto na obserwacjach mikroskopowych oraz analizie spektrofotometrycznej w podczerwieni i rentgenograficznej. Wskaźniki produktywności, wyrażone jako masa $CrO_3$ przypadająca na jednostkę masy wsadu, kształtowały się na poziomie 0,175-0,236. Zgodnie z założeniami technologicznymi fazę rozpuszczalną stanowił chromian sodu, natomiast w skład frakcji nierozpuszczalnej wchodziły takie fazy jak peryklaz, oksychromit wapnia czy krzemian dwuwapniowy. Spieki pochodzące z procesu dolomitowego zawierały dodatkowo brownmilleryt. Również inne właściwości fizykochemiczne badanych spieków były podobne, z wyjątkiem temperatur spiekania i mięknięcia.