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CHROMIC ORE PROPERTIES SIMPLIFYING THEIR CHEMICAL PROCESSING

This work presents research results which allowed to formulate the equation which determines coefficient $W_r$ as the function of the content of $\text{Cr}_2\text{O}_3$, $\text{Al}_2\text{O}_3$, $\text{SiO}_2$ and $\text{CaO}$ in chromic ore. Knowing the content of the essential component in chromic ore, i.e. $\text{Cr}_2\text{O}_3$, we calculated the value of $W_r$ for each grade of chromic ore and determined the quantity of calcium oxide which should be added to the chromate charge. Thus, it was possible to select quantities of chromate charge components without performing highly labour and time consuming analyses. Such a solution was implemented in the analytical procedure in the Alwernia Chemical Works and it reduced the frequency of chromic ore analyses to one per day.

Key words: chromic ore, analyses, chromate charge

INTRODUCTION

During the years 1999-2000, a new technology of sodium chromate production with an in-process chromic mud recycling was implemented in the Alwernia Chemical Works (Kowalski and Mazanek, 1998; Kowalski and Wantuch, 1999; Kowalski, 1990; Kowalski, 1993; Walawska and Kowalski, 2000). The new technology allowed to reduce quantity of the disposed waste by about 80% (from 4,000 to 700 kg per 1 ton of the produced sodium chromate). The emission of chromium compounds to the air was decreased to 9.5 ton per year (adjusted to overall chromium content), which meets the world level (in 1994 the emission of chromium to the air in Alwernia was higher than 300 ton per year).

The sodium chromate production process depends on the quality of raw materials used, especially chromic ore. Its chemical composition has an effect on the result of the technological process. To determine the chromic ore chemical composition, highly labour and time-consuming analyses are required. Analyse time have an essential effect on process control delaying transfer of their results.

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This work presents research results which allowed to formulate the equation which determines coefficient $W_R$ being the function of the content of $\text{Cr}_2\text{O}_3$, $\text{Al}_2\text{O}_3$, $\text{SiO}_2$ and $\text{CaO}$ in chromic ore. Knowing the content of the essential component in chromic ore, i.e. $\text{Cr}_2\text{O}_3$, we could calculate the value of $W_R$ for each grade of chromic ore.

Thus, it was possible to determine the quantity of calcium oxide which should be added to the charge and to select quantities of chromate charge components without performing highly time consuming chemical analyses which allow to find the content of silicon, aluminium and calcium compound in chromic ore. This allowed to simplify the chromate charge preparation and control of the technological process in relation to chromic ore quality.

THE SODIUM CHROMATE PROCESS WITH CHROMIC WASTE RECYCLING

The new technology of sodium chromate production (Figure 1) involves the substitution of natural raw materials with chromic waste as the waste obtained from sodium chromate production (so called chromic mud) or chromic waste consisted of hydrated chromic oxides and the use of various kinds of recycling (in-process and off-process) of chromic waste (Walawska and Kowalski, 2000 a; Walawska and Kowalski, 1999; Kowalski, 1998; Kowalski and Walawska, 2001).

The basic process node is calcination of the chromate charge (consisted of chromic ore, soda ash and chromic waste) is realised in rotary kilns at temperatures between 1423–1473 K, in an oxidising atmosphere, in the presence of a filler material, for diluting the products of the reaction. The chromite components are oxidised according to the following equation (Awierbuch and Pawlow, 1973; Nriagu and Nieboer, 1995; Papp, 1995):

$$2 \text{FeO} \cdot \text{Cr}_2\text{O}_3 + 4 \text{Na}_2\text{CO}_3 + 3,5 \text{O}_2 \rightarrow 4 \text{Na}_2\text{CrO}_4 + \text{Fe}_2\text{O}_3 + 4 \text{CO}_2$$ (1)

At the temperature of the process, both sodium carbonate ($T_1 = 1124$ K) and the sodium chromate (VI) ($T_2 = 1065$ K) being created are present in the liquid phase. Sodium chromate (VI) appears already at the temperature of 873 K as a product of the reaction running in the solid phase. At the temperature of 928 K, it forms a liquid eutectic mixture $\text{Na}_2\text{CrO}_4 - \text{Na}_2\text{CO}_3$, containing 62.5% of $\text{Na}_2\text{CrO}_4$. The presence of the liquid phase makes it difficult for oxygen to access the grains of the ore which have not reacted yet, decreasing the reaction rate, which in turn depends on the speed of the diffusion of oxygen from the air through a liquid layer of alloys surrounding the chromite grains. In order to increase the rate of the oxidising process, increasing the surface of the solid phase decreases the thickness of the alloy layer. This is achieved by using finely ground fillers. In the old standard method, dolomite was used as filler, while the new implemented method uses dried chromic mud as filler.
Fig. 1. Flow sheet of the sodium chromate production process with chromic mud and other chromic waste recycling.

The raw chromium containing materials with high content of chromium (III) usually contain such pollutants as Fe₂O₃, SiO₂ and Al₂O₃. The addition of calcium oxide fixes them into compounds hardly soluble in water according to the following reactions:
2 CaO+SiO$_2$ $\rightarrow$ Ca$_2$SiO$_4$  \hspace{1cm} (2)

3 CaO+SiO$_2$ $\rightarrow$ 3CaO·SiO$_2$  \hspace{1cm} (3)

4 CaO+Al$_2$O$_3$+Fe$_2$O$_3$ $\rightarrow$ 4 CaO·Al$_2$O$_3$·Fe$_2$O$_3$  \hspace{1cm} (4)

The produced sinter is leached in water. During leaching, Na$_2$CrO$_4$ is dissolved in water. The suspension obtained in the leaching process is filtrated. The filtrate containing a solution of Na$_2$CrO$_4$ is a product. The precipitate from the filtration (chromic mud) is pulped with water and filtrated once more. The product from the second filtration is reused in the leaching process.

After filtration, the moist chromic mud (containing 30–40 % of H$_2$O content) is divided, in a suitable proportion, into two streams; one stream is transported to the waste material storage, and the other is returned to the process after desiccation.

The target solution provides the exploitation of the existing old chromic heaps and dry enrichment of chromic waste from the existing storage. This process permits increasing the content of chromium in the chromic waste recovered to the process using the grain classification, which increases the content of chromite in recovered fractions (Walawska and Kowalski, 2000 a).

**SELECTION OF THE CHROMATE CHARGE COMPOSITION**

Research on the chemical and physical composition of the chromate sinter showed that the sinters coming from the dolomite method and from the process with chromic mud recycling have practically the same phase composition. They contain sodium chromate alloy, unreacted chromic ore, brownmillerite 4CaO·Al$_2$O$_3$·Fe$_2$O$_3$ and calcium silicate $\beta$-Ca$_2$SiO$_4$, Ca$_3$SiO$_3$ (Kowalski, 1990). Calcium silicates and brownmillerite are water insoluble, but during leaching of the chromate sinter they are the subject of complicated hydrolysis reactions. The absence of calcium silicates and brownmillerite in the chromate sinter results in the transition of silicon and aluminium compound into sodium chromate solution in the form of water-soluble silicates and aluminates. Full quantitative processing of the silicate and aluminates with calcium oxide is very important for the production of a high quality sodium chromate solution. As a result, it is necessary to add CaO to the chromate charge.

The recycled chromic mud contains high quantities of sodium and calcium compounds and unreacted chromic ore, which are the subject of analogical reactions as natural chromic ore, soda ash and calcium oxide, added to the chromate charge. They involve some changes in the soda ash and calcium oxide quantities added to the chromate charge.

Research on the composition of the chromate sinter and chromic mud allows to formulate the equations determining the composition of the chromate charge (Kowalski, 1990; Kowalski and Walawska, 2001). These equations determine the
relationship between such raw materials added to the charge as chromic ore, soda ash, calcium oxide, chromic mud and the chemical composition of chromic ore. It also made an assumption that quantity of the used CaO should be sufficient to chemically bind SiO₂ from the chromic ore into calcium orthosilicate and Al₂O₃ and FeO from the chromic ore into brownmillerite. The calculation of the chromic ore quantity added to the charge takes into account the unreacted chromic ore in chromic mud. The final equations are as follows:

\[ R + S + W + Ar = 1000 \] 
\[ x = \frac{R \cdot Cr_2O_3(R) + Ar \cdot Cr_2O_3(Ar)}{100} \]
\[ a = \frac{W}{CaO_{(stech.)}} \]
\[ b = \frac{S}{Na_2CO_3_{(stech.)}} \]
\[ CaO_{(stech.)} = R \cdot [Cr_2O_3(R) - W_R - 1] + [Cr_2O_3(Ar) \cdot Ar/Cr_2O_3(R)] \cdot [Cr_2O_3(R) - W_R - 1] \]
\[ Na_2CO_3_{(stech.)} = 0.01395[R \cdot Cr_2O_3(R) + Ar \cdot Cr_2O_3(Ar)] \]

where: \( R \) (chromic ore or tannery waste), \( Ar \) (chromic mud), \( S \) (soda), \( W \) (calcium oxide) - quantities of raw materials [kg/1000kg of charge]; \( Cr_2O_3 - \% Cr_2O_3 \) in \( Ar \) or \( Gr \); \( X, a, b, CaO_{(stech.)}, Na_2CO_3_{(stech.)} \), \( W_R \), indicators (described below).

- Coefficient \( a \) is the stoichiometric indicator of calcium oxide, which is a ratio of the mass of calcium oxide \( W \) used in the process and the stoichiometric mass \( CaO_{(stech.)} \) resulting from equations (2-4).
- Coefficient \( b \) is the stoichiometric indicator of sodium carbonate, which is a ratio of the mass of the sodium carbonate used in the process \( S \) and the stoichiometric mass \( Na_2CO_3_{(stech.)} \) resulting from reaction (1).
- Coefficient \( X \) defines chromium content in the charge (as \% \( Cr_2O_3 \)).
- Coefficient \( W_R \) is connected with the chemical composition of chromic ore (see: next point).

The analytical control of raw materials used in the sodium chromate process includes chemical analyses of chromic ore, soda ash, burned lime and dried chromic mud. A set of analytical procedures which contain methods provided by quality assurance system PN-ISO 9002:1996 were presented in works (Kania and Kotowicz, 1998; Przepisy analityczne, 1998).
THE SIMPLIFICATION OF THE CHEMICAL ANALYSES OF CHROMIC ORE AS THE CONSEQUENCE OF USING $W_R$ EQUATION

The new technology allowed to use different grades of chromic ore (especially those from Kazakhstan, South Africa and Turkey). The chemical composition of the chromic ore is not stable. Its basic component is chromite ($\text{Cr}_2\text{O}_3 \cdot \text{FeO}$) but chromic ore content also included complex hydrated magnesium and aluminium aluminosilicate, magnesite, opal ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$), serpentine [Mg$_3$Si$_2$O$_5$(OH)$_4$], sometimes ferric hydroxide and low content of Ca, Zn, Mn, V, S, P compounds (Avierbuch and Pawlów, 1973; Papp, 1995). This rather wide mineral composition caused some difficulties in the preparation of the chromate charge. Unfortunately, the total chemical analysis of the chromic ore allowing to determine $\text{Cr}_2\text{O}_3$, $\text{SiO}_2$, $\text{Al}_2\text{O}_3$, FeO, SiO$_2$ and CaO content is highly labour and time consuming and there is no possibility to use it as an operating analysis. Total analyses of the average proof of chromic ore should be performed for each raw material lot supplied to the process. This is required by the quality assurance system (Kania and Kotowicz, 1998).

Presented in equation (9), coefficient $W_R$ is a linear function of the content of $\text{Cr}_2\text{O}_3$, $\text{SiO}_2$, $\text{Al}_2\text{O}_3$ and CaO in chromic ore.

$$W_R = \frac{(100 \cdot \text{Cr}_2\text{O}_3) - 100 - 1.9 \cdot \text{SiO}_2 - 2.2 \cdot \text{Al}_2\text{O}_3 - \text{CaO}_R}{100}$$

where: $\text{Cr}_2\text{O}_3$ - % of $\text{Cr}_2\text{O}_3$ in the chromic ore; $\text{Al}_2\text{O}_3$ - % of aluminium compound (expressed as $\text{Al}_2\text{O}_3$) in the chromic ore; $\text{SiO}_2$ - % of silicone compound (expressed as $\text{SiO}_2$) in the chromic ore; $\text{CaO}_R$ - % of calcium compound (expressed as CaO) in the chromic ore; 1.9 and 2.2 stoichiometric coefficients follow from equations (2,4).

Equation (11) could be expressed as:

$$W_R = a \cdot \text{Cr}_2\text{O}_3 - b$$

where: $a$ and $b$ are linear coefficients of the straight line and $b$ is determined by the equation:

$$b = -(1.9 \cdot \text{SiO}_2 + 2.2 \cdot \text{Al}_2\text{O}_3 - \text{CaO}_R)$$

It was assumed that typical chromic ore from the analysed deposit should have a stable proportion of silicon, aluminium and calcium compounds. This way, the value of equation (13) linear coefficient should be constant for each chromic ore grade. Possible differences in the content of silicon, aluminium and calcium compounds in different chromic ore grades should also be distinguished by the change of „$b$“ and „$a$” values. If equation (11) is valid for each grade of the chromic ore, it is possible to determine the composition of chromate charge, using only the results of the analyses.
of the main component of the chromic ore, i.e. Cr₂O₃. W_R value could be calculated (knowing coefficients “a” and “b”) from equation (11) or taken from the W_R diagram. According to equation (9), the calculated W_R value allows to estimate the CaO quantity which should be added to the chromate charge without determining the SiO₂, Al₂O₃ and CaO(R) content in chromic ore. To check this hypothesis, analyses were performed on representative proofs of the three typical chromic ores used in Poland to the sodium chromate production (Turkish, Kazakh and South-African). Table 1 presents the analytical results and calculated W_R values.

<table>
<thead>
<tr>
<th>Chromic ore grade and proof number</th>
<th>Content of component [%]</th>
<th>W_R value calculated according equation (11)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cr₂O₃</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Kazakh chromic ore</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>40.8</td>
<td>12.7</td>
</tr>
<tr>
<td>2</td>
<td>44.6</td>
<td>13.4</td>
</tr>
<tr>
<td>3</td>
<td>46.8</td>
<td>11.2</td>
</tr>
<tr>
<td>4</td>
<td>49.1</td>
<td>6.8</td>
</tr>
<tr>
<td>5</td>
<td>51.6</td>
<td>10.2</td>
</tr>
<tr>
<td>6</td>
<td>53.8</td>
<td>13.1</td>
</tr>
<tr>
<td>Turkish chromic ore</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>45.7</td>
<td>7.5</td>
</tr>
<tr>
<td>2</td>
<td>47.6</td>
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</tr>
<tr>
<td>3</td>
<td>48.5</td>
<td>10.6</td>
</tr>
<tr>
<td>4</td>
<td>49.1</td>
<td>17.1</td>
</tr>
<tr>
<td>5</td>
<td>50.2</td>
<td>15.5</td>
</tr>
<tr>
<td>South African chromic ore</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>43.7</td>
<td>19.8</td>
</tr>
<tr>
<td>2</td>
<td>44.2</td>
<td>17.3</td>
</tr>
<tr>
<td>3</td>
<td>45.22</td>
<td>21.3</td>
</tr>
<tr>
<td>4</td>
<td>45.8</td>
<td>16.3</td>
</tr>
<tr>
<td>5</td>
<td>45.89</td>
<td>17.93</td>
</tr>
</tbody>
</table>

Figures 1-3 present the diagram of the relationship of the W_R value and Cr₂O₃ content in Turkish, Kazakh and South African chromic ore. As a result of the linear regression, a linear equation for Kazakh (14), Turkish (15) and South African (16) chromic ore was obtained.

\[ W_R = 1.012 \cdot Cr_2O_3 - 1.93999 \]  
(14)
\[ W_R = 0.973565 \cdot \text{Cr}_2\text{O}_3 - 0.0971196 \]  \hfill (15)

\[ W_R = 1.02353 \cdot \text{Cr}_2\text{O}_3 - 2.48522 \]  \hfill (16)

Fig. 1. Relation of the \( W_R \) value and \( \text{Cr}_2\text{O}_3 \) content in Kazakh chromic ore

\[ Y = 1.012 \cdot X - 1.93999 \]

Fig. 2. Relation of the \( W_R \) value and \( \text{Cr}_2\text{O}_3 \) content in Turkish chromic ore

\[ Y = 0.973565 \cdot X - 0.0971196 \]
The presented results confirmed the linear relationship $W_R = f(Cr_2O_3)$ for the three analysed grades of the chromic ore originating from different deposits of this raw material. Consequently, chemical analyses of the milled chromic were limited to determinate of the $Cr_2O_3$ content only. Such a solution was implemented in the Alwernia Chemical Works. According to (Przepisy analityczne, 1998) the $Cr_2O_3$ content in an average proof of chromic ore is determined with the redoximetric method once per day.

CONCLUSIONS

The new sodium chromate production technology with chromic mud recycling allowed to use different grades of chromic ore (especially the ones from Kazakhstan, South Africa and Turkey). This caused some difficulty in preparation of the chromate charge, which is especially important for the process with chromic mud recycling in which quantity of the used CaO should be sufficient to chemically bind SiO₂, Al₂O₃ and FeO from the chromic ore into a water insoluble compound. Unfortunately the total chemical analysis of the chromic ore is the high time consuming and there is no possibility to use it as an operating analysis.

Research results allowed to formulate the equation which determined coefficient $W_R$ as being the function of the content of the $Cr_2O_3$, $Al_2O_3$, SiO₂ and CaO in chromic ore. Knowing the content of the chromic ore main component, i.e. $Cr_2O_3$, we were able
to calculate the value of the $W_R$ for each grade of chromic ore and determine the calcium oxide quantity which should be added to the chromate charge. This way, it was is possible to select quantities of chromate charge components without performing chemical analyses, which simplified chromate charge preparation and the control of the technological process in relation to chromic ore quality.

The presented result confirmed a linear relationship $W_R = f(Cr_2O_3)$ for three analysed grades of the chromic ore which originated from different deposits of this raw material. In consequence, chemical analyses of the milled chromic were limited to the determination of the $Cr_2O_3$ content only. Such a solution was implemented in the Alwernia Chemical Works.

REFERENCES


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Technologia produkcji chromianu sodu dopuszcza możliwość wykorzystania różnych rodzajów rudy chromowej (kazachska, turecka, południowoafrykańska). Całkowita analiza rudy chromowej na zawartość $Cr_2O_3$, $SiO_2$, $Al_2O_3$, $FeO$ i $CaO$ jest niestety czynnością bardzo czasochlonną i w związku z tym, nie może spełniać roli analizy międzyoperacyjnej. Stwarza to trudności w zestawianiu mieszanek wsadowych, zwłaszcza w metodzie z recyrkulacją błota pochromowego, gdzie zawartość $CaO$ w
mieszance musi zapewnić związek związków glinu, żelaza i krzemu zawartych w rudzie w postać związków nierozpuszczalnych w wodzie. Wyniki badań pozwoliły na opracowanie formuły określającej współczynnik \( W_R \) będący funkcją zawartości w rudzie \( \text{Cr}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{SiO}_2 \) i \( \text{CaO} \). Znając zawartość głównego składnika rudy chromowej, tj. \( \text{Cr}_2\text{O}_3 \), można określić wartość \( W_R \) dla dowolnej rudy chromowej i stosując odpowiedni wzór wyliczyć ilość tlenku wapnia, którą należy dodać do wasadu chromianowego. Dzięki temu stało się możliwe dobieranie ilości składników wasadu chromianowego bez wykonywania żmudnych analiz na zawartość związków krzemu, glinu i wapnia w rudzie chromowej. Uprościło to znacznie zestawianie składania wasadu chromianowego i sterowania procesem technologicznym zależnym od jakości rudy chromowej i umożliwiło ograniczenie ilości analiz rudy chromowej w Zakładach Chemicznych Alwernia do jednej na dobę wykonywanej ze średniej próbki.