

Selection of Technological Variants of Sodium Chromate (VI) Production Process with the Use of Chromic Waste

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Abstract

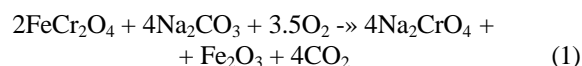
Various variants of the technological concept of using chromic waste as a substitute of natural raw materials, i.e. chromium ore and dolomite, in the standard process have been proposed. The object (process) function, valid in the researched area, was determined by assuming material balance equations (which describe each of the above-mentioned technological nodes) and by using the relations determined on the basis of experiment results. To work out this function the collections of values characterizing this function and a classification of these values were created.

Keywords: sodium chromate, chromic waste, utilization

Introduction

Wastes containing chromium are created in many branches of industry. During the last 50 years of production of chromium compounds in Poland, over 3 million tons of waste chromic materials have been amassed on the heaps in the "Alwernia" Chemical Works near Cracow. A further 1.5 mln tons are stored on the heap of the former producer of ferrochromium in Siechnice. It was also evaluated that on other - both permanent and temporary heaps - more than 0.5 mln tons of tannery and galvanic solid wastes are stored [1-5].

This work presents the results of investigations on elaboration of different variants of the technology of using chromic solid waste as a substitute for natural raw materials - such as chromium ore and dolomite - which are used in the standard process of producing sodium chromate (VI). Sodium chromate is the basic intermediate product, from which all the other chromium compounds are produced. The standard sodium chromate (VI) production process [6-8] is based on calcination of the mixture of chromium ore, soda and dolomite, in rotary furnaces, at the temperature of 1423-1473 K, in the oxidizing atmosphere. The chromite components are oxidized according to the following equation:



Using dolomite as a filler causes this method to be characterized by a low process efficiency (about 70%) and a big quantity of the created waste [6, 7, 9], which can reach even 4 tons of damp "chromic mud" per 1 tonne of product. The total chromium content in such waste material can reach 15 mass % of Cr_2O_3 . From the mineralogical point of view, chromic mud is a very complex multicomponent system, with variable quantitative composition of each mineral phase [10-12].

Research on methods of obtaining sodium chromate(VI) has been carried out for a long time. At present, the biggest producers in the world use the technology with dried and ground mud used as a filler [8,13, 14]. In Poland, a number of works have been conducted where the dolomite filler was substituted by another, resulting in a decrease of the final quantity of waste [4, 9, 15, 16]. Works on using chromic mud recycling [17, 18] were also carried out.

Solid chromic waste existing in Poland, which can be used in the process of obtaining sodium chromate(VI), can be divided into three groups: - Wastes which are obtained in production of chromium

compounds in the Chemical Works "Alwernia". In 1997, their quantity was about 50,000 tonnes per year [39]: about 47,000 in the form of chromic mud and 3,000 in the form of hydrated chromium oxides.

- Galvanic and tannery wastes, containing hydrated chromium(III) oxides, of which Cr(III) content (depending on occurrence) is 5-15%, and about 70% water [20-22]. Sometimes, these wastes also contain significant quantities of organic compounds (wastes from the tannery sewage treatment plants). Their quantities are estimated at the level of 18,000-20,000 tonnes per year [26, 23].
- Leather wastes, containing 3-7% Cr(III), obtained in the chromic tanning process, as well as production of shoes and leather fancy goods (scraps). Their quantities are estimated at the level of about 40,000 tonnes per year [24-26].

Selection of the Technological Variants

The new technological conception of sodium chromate(VI) production takes into consideration the substitution of natural chromium raw materials with chromic wastes and the use of various kinds of recycling (in-process, on-site, off-site) of chromic waste. That enables multivariant conducting of the process [5, 27-32]. These variants however, have common technological nodes. A principle that a maximum number of unitary technological operations will be realized in each node was accepted, with the exception of such operations, which could eliminate the variables controlling the process. The set of nodes was minimal in that each attempt at its reduction would require an introduction of additional controlling variables, which would be undesirable due to the increasing dimensionality of the researched optimization problems. The following set of basic process nodes has been determined (Fig. 1).

Node 1. Charge Preparing

This node is present in each analyzed variant, and it includes all the operations involved in the preparation of raw materials: drying, grinding, weighing and mixing.

Sodium carbonate, calcium oxide and chromium-containing raw material with a high Cr content (above 45% of Cr_2O_3), (chromium ore or tannery waste), as well as chromium-containing raw material with a low chromium content (below 20% of Cr_2O_3), (chromic mud and chromic waste from the storage heap used as the so-called fillers), are used as raw materials in each of the variants.

Node 2. Obtaining Sodium Chromate(VI)

That is the main technological node in the process (Fig. 2). In the calcination process, both sodium carbonate and Na_2CrO_4 , exist in a liquid phase. The main cause of formation of a significant quantity of liquid is also the creation of bicomponent eutectic systems: $Na_2CrO_4-Na_2CO_3$ and $Na_2CrO_4-Na_2SiO_3$. The rate of oxidation process depends on the speed of diffusion of air

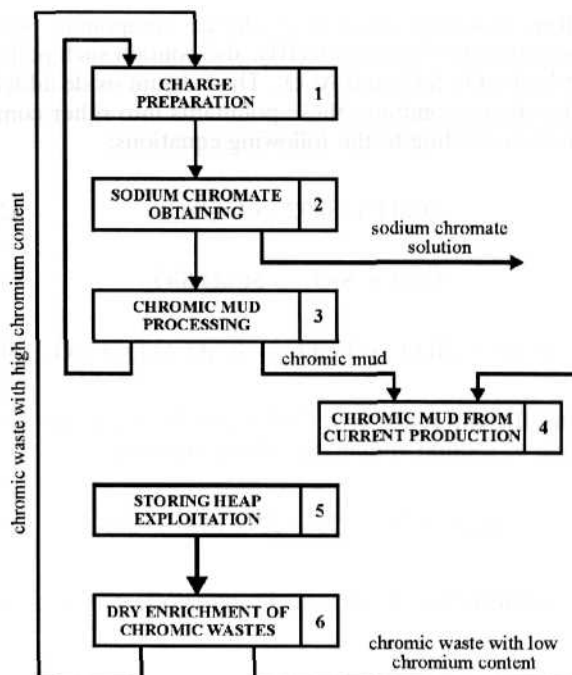


Fig. 1. Schema of basic nodes connections of the sodium chromate (VI) producing process.

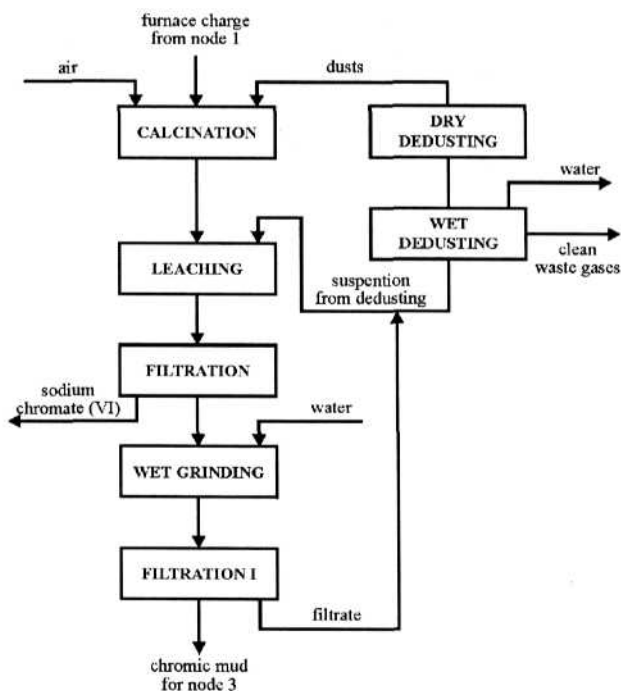
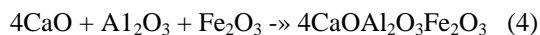
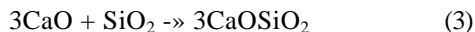


Fig. 2. Node 2 - sodium chromate(VI) obtaining.

oxygen - through a liquid layer of alloys, surrounding chromite grains - in direction of its surface. In order to increase the rate of oxidation process, the thickness of the layer must be decreased, by the use of fillers, such as dolomite or chromic waste materials with low chromium(III+VI) content [6-8].

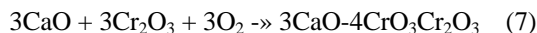
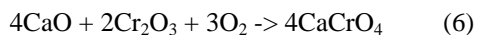
Raw materials used as a charge component with a high content of chromium(III), also contain such pollutants as Fe₂O₃, SiO₂ and Al₂O₃. The calcium oxide added to the charge combines these pollutants into other compounds, according to the following equations:



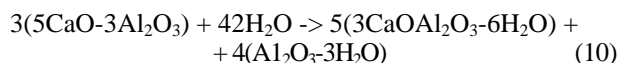
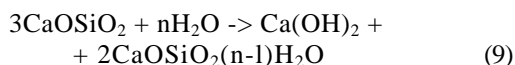
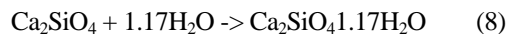
Insufficient quantity of CaO is conducive to the formation of sodium aluminate, soluble in water:



The formation of calcium chromate(VI) was also observed:



The sinter obtained in the calcination process is leached in water. During leaching the Na₂CrO₄ which is formed is dissolved in water, and the other components of the solid phase can be hydrated according to the following reactions:



The suspension, obtained in the leaching process, is filtrated. The filtrate, containing a solution of Na₂CrO₄, is a product. The precipitate from the filtration is pulped with water and filtrated once more. The filtrate from the second filtration is used in the leaching process.

Node 3. Chromic Mud Processing

The dump chromic mud is divided into two streams. The first is transported to the storage heap and the second one is returned to the process after drying.

Node 4. Storing of the Chromic Mud Obtained in the Current Production

This is a stipulated node, symbolizing the storage of the chromic mud obtained in the current production of sodium chromate(VI), on a heap of chromic waste.

Node 5. Exploitation of the Existing Chromic Waste Storage Heap

A stipulated node, introduced for discerning the chromic mud created in the current production, from the old chromic waste materials stored on the heaps and taken to the production process.

Node 6. Dry Enrichment of Chromic Waste Materials

In this node, the operation of drying and dry enrichment takes place. The contents of Cr(III + VI) in chromic waste materials from the storing heap can be increased with the use of dry enrichment, by separating fractions with a higher Cr(III) content, by grain classification. The result of the enrichment depends on the initial contents of Cr(III). Because of that, only dry enrichment of such waste materials from chromium storage heaps, in which the initial Cr(III) content was significantly higher (> 8 mass % Cr₂O₃) than in chromic mud from the process, was accepted in the analysis of technological concepts, [9, 30, 33-36].

On the basis of the process analysis [6, 29, 33] and our own investigations [30, 37-39], two groups of technological variants were set apart. They differ in terms of the kind of chromium containing raw materials (with a high Cr content) used: A - chromium ore, B - tannery wastes.

Taking into consideration the connections of basic nodes (Fig. 1), technological solutions of the process of obtaining Na₂CrO₄ within these variants have been determined (Fig. 3).

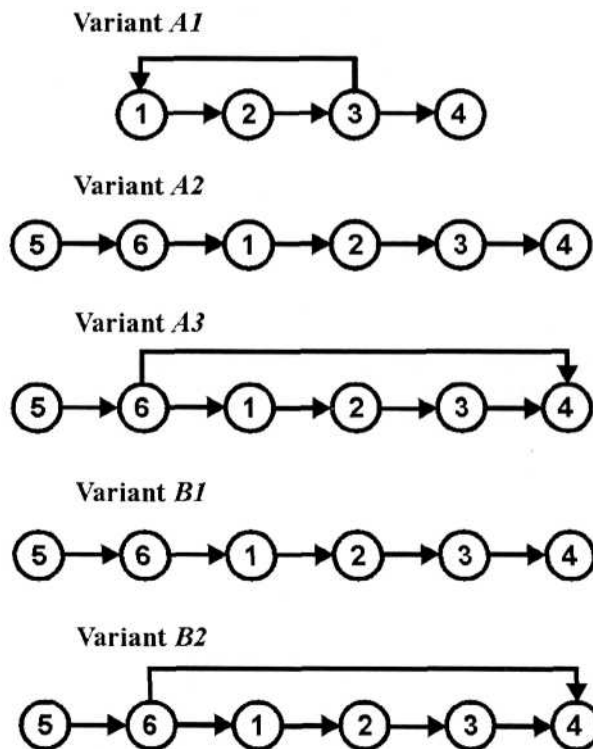


Fig. 3. Technological variants of sodium chromate(VI) production — connections of nodes.

The variant of *A1* is the simplest. It comprises obtaining Na_2CrO_4 by in-process recycling of a part of dry chromic mud, which is used as a filler. The other part of the waste is transported onto a storage heap. This solution - in comparison with the standard dolomite method - should considerably reduce the quantity of chromic mud stored on the heaps.

In the *A2* variant, the process is conducted by using on-site recycling of chromic waste from the existing heap, which - after drying - is used as a filler. The damp chromic mud from the process is transported onto the storage heap. Such a solution is especially profitable when the contents of Cr(III+VI) in the chromic waste from the heaps is much higher than its contents in chromic mud obtained in the process. This will result in decreasing the chromium ore consumption coefficient.

In the *A3* variant, on-site recycling is also used, but the chromic waste from the existing storage heap is additionally dryly enriched. The enriched fraction, with high Cr(III) contents, is used as a filler. The residue is transported to the heap - together with the chromic mud formed in the process. Because of high contents of Cr(III+VI) in the chromic waste from the heap and of a high enrichment level, it is possible to decrease the chromium ore consumption coefficient even further.

When tannery wastes were used, the variants using in-process recycling were given up, because in that method the amount of chromic mud, which is formed in the process, and is necessary as a filler, [39] is insufficient.

The *B1* variant provides on-site and off-site recycling of chromic wastes. The chromic waste from the existing heap, after drying, is used in the process. The damp chromic mud, which is formed in the process, is transported to the heap. Because of the high contents of Cr(III+VI) in the waste introduced to the process, its mass will be bigger than the mass of chromic mud produced in the process.

In the *B2* variant, the previous technological solution was extended with the node of dry enrichment of the waste taken from the existing heap. This waste, after drying, is enriched by separating of fraction of higher contents of Cr(III+VI). This fraction is then introduced to the process together with tannery waste. This solution when high contents of Cr(III) are observed in the chromic waste as an effect upon the enrichment level, will increase the difference between the mass of chromic waste that is introduced to the process and the mass of chromic mud produced in the process.

Object Function Identification

Production of sodium chromate(VI) is a complex process. During the calcination process many reactions, as well as physical and chemical processes, take place which have not yet been thoroughly examined. Working out a deterministic mathematical model consistent with the real process was acknowledged as being impossible. Therefore, experimental and statistical methods were used for its identification. In defining the object function, valid in the investigated area, a system of material balance equations was accepted as the base. The equations

describe each of technological nodes presented above by using relations, which were defined on the basis of experiment results [37-39]. In order to work out this function, it was necessary to prepare a set of values characterizing it and their classification.

The independent process parameters were parameters which were useful for controlling the process. For the examined object of research the following process parameters were accepted:

- *a* - stoichiometric indicator of calcium oxide, which is a ratio of the mass of calcium oxide used in the process, to the stoichiometric mass resulting from reactions (2) and (4):

$$a = \frac{t}{\text{CaO}_{(\text{stech})}} \quad (11)$$

From the analysis of the compositions of the charge in the calcination process [37-39], it was accepted that the range of change of this variable will be $a \in (0.2; 1.0)$.

- *b* - stoichiometric indicator of sodium carbonate, which is a ratio of the mass of the calcium carbonate used in the process, to the stoichiometric mass resulting from the reaction (1):

$$b = \frac{s}{\text{Na}_2\text{CO}_{3(\text{stech})}} \quad (12)$$

In industrial units this indicator is usually below 1.0. In the dolomite method it is equal to 0.9-0.95 [6-8], and in the process where chromic mud is recycled it can even be smaller [37-39]. This is the result of the presence of a sodium ion in the recycled waste. The accepted range of changes for this variable was $b < 0.5; 1.0 >$.

- *X* - chromium contained in the charge, calculated to Cr_2O_3 [mass %]. This variable bonds the mass of the chromium containing raw materials used, with their contents of Cr(III+VI). According to [6, 9], the use of either excessive values of *X* (> 19.5 of mass %), or too little *X* values (< 10.5 mass %), decreases the output of Na_2CrO_4 production process. In the dolomite method, Cr_2O_3 content in the charge equals to 16.5 mass %. In modern installations it is endeavoured to lower its content [39]. The accepted range of changes for this variable was $X < 10.5; 19.5 >$.

The dependent technological parameters were defined on the basis of the results of the experiment. For the examined object, as output values, the following values of mass % of Cr^{Oj} content in chromic mud were accepted: C_A^{Cr} , C_A^{CrNa} , C_A^{Crk} .

The values of constant parameters were accepted for industrial installation imitating conditions in the "Alwernia" Chemical Works. These are the following values:

- *grain size of used raw materials* - The influence of grain size of different kinds of chromium ore upon obtaining Na_2CrO_4 , determining the velocity of heterogeneous reactions, connected with the surface of phase contact, is well-known [34-36]. In research, chromium ore of grain-size $< 75 \mu\text{m}$ was used.

- *temperature distribution during calcination* - Factors such as temperature, the time of calcination, as well as temperature changes in time, exert a significant influence on the sodium chromate(VI) production process. When

the charge is heated up to the calcination temperature too quickly it melts [6-9]. In our laboratory research, a calcination time of 2.5 hours was accepted, and during it suitable temperature discipline was maintained [39].

- *time and temperature of leaching* - These parameters influence the level of elution of Na_2CrO_4 from the chromic mud. A leaching time of 2 hours and temperature of 353-373 K were accepted.

- *solid phase content in the leached suspension* - 20-25 mass % of solid phase was accepted.

The process was described with balance equations, which characterized the solid phase in the fixed state for each of the examined nodes, as a function of the accepted process parameters (a, b, X).

Node 1 - Charge Preparation

On the basis of the law of conservation of mass, the total balance of node 1 can be presented as the following:

$$G_p - G_k = 0 \quad (13)$$

In order to facilitate the calculations, it was accepted that $G_k = 1$.

Mass of the substances introduced to node 1, was equal to the sum total of the masses of the raw materials used. The mass balance for node 1 was defined in the following way:

$$1 - [s(a, b, X) + t(a, b, X) + \sum_{i=1}^n w_i(a, b, X)] = 0 \quad (14)$$

Total chromium mass, in the mixture going out from the node, is equal to the mass of chromium introduced with chromium-containing raw materials. The partial balance of Cr(III+VI), has been presented as the following:

$$X - \sum_{i=1}^n w_i(a, b, X) \cdot C_i^{Cr} = 0 \quad (15)$$

Raw materials consumption was calculated based on equations (1), (2) and (4). The mass of Na_2CO_3 was determined, taking into consideration the presence of sodium in chromium-containing raw materials - i.e. in tannery waste materials.

$$s(a, b, X) = b \cdot [\alpha \cdot \sum_{i=1}^n w_i(a, b, X) \cdot C_i^{Cr} - \beta \cdot \sum_{i=1}^n w_i(a, b, X) \cdot C_i^{Na}] \quad (16)$$

The mass of calcium oxide was defined from equations (2) and (4), decreasing it by the mass of the CaO present in other raw materials. The CaO mass fraction was calculated from the equation written below:

$$t(a, b, X) = \alpha \cdot [\chi \cdot \sum_{i=1}^n w_i(a, b, X) \cdot C_i^{Si} + \sigma \cdot \sum_{i=1}^n w_i(a, b, X) \cdot C_i^{Al} - \mu \cdot \sum_{i=1}^n w_i(a, b, X) \cdot C_i^{Ca}] \quad (17)$$

In the case of using chromium ore, the CaO mass fraction in the charge can be determined when the indicator $W^R C_1^{Cr} = 1.01181 \cdot C_1^{CrR} - 1.93791$ is known [9]. This indicator was defined on the basis of chromium C_1^{Cr} content in the chromium ore.

$$t(a, b, X) = a \cdot w_1(a, b, X) \cdot [C_1^{CrR} - W^R C_1^{Cr} - 1] \quad (18)$$

For the sake of simplicity, it was accepted that the total chromium contained in the chromium containing raw material "i", is the sum of the contents of chromium (III) and chromium(VI) [9]:

$$C_i^{CrR} = C_i^{Crk} + C_i^{CrR} \quad (19)$$

It was also accepted that the contents of Cr(VI), soluble in H_2SO_4 , in the "i" chromium containing raw material are the sum of Cr(VI) soluble in water (Na_2CrO_4) and soluble only in the acid CaCrO_4 .

$$C_i^{CrR} = C_i^{CrNa} + C_i^{CrCa} \quad (20)$$

Node 2 - Obtaining of Sodium Chromate (VI)

Calcination

Change of the mass was calculated as the difference of the mass of the solid phase going out from the calcination process, and that introduced to it, with the raw materials from node 1:

$$\begin{aligned} [s(a, b, X) + t(a, b, X) + \sum w_i(w_i(a, b, X))] = \\ = F(a, b, X) + z \cdot \Delta F(a, b, X) \end{aligned} \quad (21)$$

On the basis of analysis of the calcination process, it was assumed that mass change is mainly the result of the way the chemical reactions (1), (6) and (7) run, of carbonate decomposition and of the dehydration process.

$$\Delta F(a, b, X) = \Delta r(a, b, X) + \sum \Delta w_i \cdot w_i(a, b, X) \quad (22)$$

Change of the mass in the chromium-containing raw material "i", during calcination, was determined by roasting it at a temperature of 1423 K for 2.5 h. The change was calculated from the following equation:

$$\Delta w_i = \frac{w_i - w_{ik}}{w_i} = \frac{w_i(a, b, X) - w_{ik}(a, b, X)}{w_i(a, b, X)} \quad (23)$$

The solid phase mass change - being the result of reactions (1), (6) and (7) - is the effect of a difference between the mass of the educed carbon dioxide, and the mass of oxygen absorbed from the air.

$$\Delta r(a, b, X) = m^{CO_2}(a, b, X) - m^{O_2}(a, b, X) \quad (24)$$

The quantity of the educed CO_2 - resulting from the decomposition of Na_2CO_3 - was determined from equation (1):

$$m^{CO_2}(a, b, X) = \phi \cdot s(a, b, X) \quad (25)$$

The oxygen mass was defined as a sum of its mass used in reaction (1), decreased by the mass, which is necessary to obtain $CaCrCO_4$ - according to the reactions (6) and (7):

$$m^{O_2}(a, b, X) = \gamma \cdot [(m_k^{Na_2CrO_4}(a, b, X) - M_p^{Na_2CrO_4}(a, b, X)) + (m_k^{CaCrO_4}(a, b, X) - m_p^{CaCrO_4}(a, b, X))] \quad (26)$$

The mass of Na_2CrO_4 introduced to the calcination process was calculated from its content in the chromium-containing raw materials used - according to the following equation:

$$m_p^{Na_2CrO_4}(a, b, X) - \mu \cdot \sum w_i(a, b, X) \cdot C_i^{CrNa}$$

The mass of $CaCrO_4$, introduced with the raw materials was determined in a similar fashion:

$$m_p^{CaCrO_4}(a, b, X) = \mu \cdot \sum_{i=1}^n w_i(a, b, X) \cdot (C_i^{Crk} - C_i^{CrNa}) \quad (28)$$

The mass of Na_2CrO_4 in the calcinated sinter was a sum of the mass of the product $P(a, b, X)$ (Na_2CrO_4 soluble in H_2O), and its quantity left in the chromic mud $A(a, b, X)$:

$$m_k^{Na_2CrO_4}(a, b, X) = \kappa \cdot P(a, b, X) + m \cdot A(a, b, X) \cdot C_A^{CrNa} \quad (29)$$

The $CaCrO_4$ mass was determined from its content in the chromic mud as the following:

$$m_k^{CaCrO_4}(a, b, X) = \mu \cdot A(a, b, X) \cdot (C_A^{Crk} - C_A^{CrNa}) \quad (30)$$

In order to simplify the equations, some additional parameters were introduced. These were the decomposition degree and the degree of oxidation of Cr(III). These parameters determine the degree of transformation of Cr(III) into Cr(VI) in the calcination process.

Decomposition degree u_r , according to [6], is the ratio of the mass of obtained Na_2CrO_4 and the mass of introduced Cr(III):

$$u_r = \frac{m_k^{Na_2CrO_4}(a, b, X) - m_p^{Na_2CrO_4}(a, b, X)}{\mu \sum_{i=1}^n w_i(a, b, X) \cdot C_i^{CrR}} \quad (31)$$

After substituting equations (27) and (29), the decomposition degree has been defined as the following:

$$u_r(a, b, X) = \frac{\frac{\kappa}{\mu} \cdot P(a, b, X) + A(a, b, X) \cdot C_A^{CrNa}(a, b, X)}{\sum_{i=1}^n w_i(a, b, X) \cdot C_i^{CrNa}} + \frac{\sum_{i=1}^n w_i(a, b, X) \cdot C_i^{CrNa}}{\sum_{i=1}^n w_i(a, b, X) \cdot C_i^{CrR}} \quad (32)$$

The oxidation degree u_u , according to [6], has been determined as the ratio of the mass of obtained Cr(VI) to the mass of introduced Cr(III):

$$u_u(a, b, X) = \frac{m_k^{Na_2CrO_4}(a, b, X) + m_k^{CaCrO_4}(a, b, X)}{\mu \cdot \sum_{i=1}^n w_i(a, b, X) \cdot C_i^{CrR}} + \frac{m_p^{Na_2CrO_4}(a, b, X) - m_p^{CaCrO_4}(a, b, X)}{\mu \cdot \sum_{i=1}^n w_i(a, b, X) \cdot C_i^{CrR}} \quad (33)$$

Having substituted the equations (27-30), the oxidation degree was determined from the following relation:

$$u_u(a, b, X) = \frac{\frac{\kappa}{\mu} \cdot P(a, b, X) + A(a, b, X) \cdot C_A^{Crk}(a, b, X)}{\sum_{i=1}^n w_i(a, b, X) \cdot C_i^{CrR}} + \frac{\sum_{i=1}^n w_i(a, b, X) \cdot C_i^{Crk}}{\sum_{i=1}^n w_i(a, b, X) \cdot C_i^{CrR}} \quad (34)$$

When equations (25), (26), (31) and (33) were introduced to equation (24), the decrement in the mass of the solid phase, being the result of chemical reactions, was determined from the following relation:

$$\Delta r(a, b, X) = \gamma \cdot \mu \cdot (2u_r(a, b, X) - u_u(a, b, X)) \cdot \sum_{i=1}^n w_i(a, b, X) \cdot C_i^{CrR} - \phi \cdot s(a, b, X) \quad (35)$$

Leaching and filtration

Na_2CrO_4 from the sinter obtained after the calcination process is leached. Next, the liquid phase is separated from the solid phase. The solid phase mass balance of these operations can be determined as follows:

$$\frac{A(a, b, X)}{\Delta A(a, b, X)} + \varphi \cdot P(a, b, X) - F(a, b, X) = 0 \quad (36)$$

The balance of Cr(III+VI) for this node has been defined by the equation written below:

$$\kappa \cdot P(a, b, X) + \mu \cdot A(a, b, X) \cdot C_A^{Cr} - X = 0 \quad (37)$$

As in the case of chromium-containing raw materials, it was accepted that chromium existing in the chromic mud is only a sum of the contents of Cr(III) and Cr(VI), whereas Cr(VI) (acid-soluble) exists in the mud in the form of Na_2CrO_4 and $CaCrO_4$.

$$C_A^{Cr}(a, b, X) = C_A^{Crk}(a, b, X) + C_A^{CrR}(a, b, X) \quad (38)$$

$$C_A^{Crk}(a, b, X) = C_A^{CrNa}(a, b, X) + C_A^{CrCa}(a, b, X) \quad (39)$$

Node 3 - Chromic Mud Processing

The chromic mud obtained in node 2 was divided into two technological streams. The balance of this node is defined in the following relation:

$$A(a, b, X) - w_2(a, b, X) = A^c(a, b, X) \quad (40)$$

The mass of the chromic mud introduced to node 1, $w_2(a, b, X) = 0$ for these variants, in which in process recycling does not exist, *i.e.* $A(a, b, X) = A^c(a, b, X)$.

Node 6 - Dry Enrichment of Chromic Waste Material from the Existing Storage Heap

The stream coming out from the storage heap was dried and divided into two: one of high and one of low Cr(III+VI) content. The mass balance has been determined in the following relation:

$$w_3(a, b, X) + w_3^u(a, b, X) - w_{3p}(a, b, X) = 0 \quad (41)$$

The fraction degree [35] was the mass participation of the chromic waste from the storage heap, transported to node 1, in the mass of the input to node 6:

$$\eta_d = \frac{w_3(a, b, X)}{w_{3p}(a, b, X)} \quad (42)$$

The total mass of waste material used in dry enrichment was equal to:

$$w_{3p}(a, b, X) = \sum_{j=1}^k w_3^j(a, b, X) \quad (43)$$

The contents of Cr(III+VI) in the educed fractions were different. The mass of chromium, introduced to this node, was equal to the sum of the masses of Cr(III+VI) in each of the educed fractions:

$$w_{3p}(a, b, X) \cdot C_{3p}^{Cr} = \sum_{j=1}^k w_3^j(a, b, X) \cdot C_3^{Crj} \quad (44)$$

The mass of the waste stream directed to node 1 was the sum of the masses of educed fractions, with a higher Cr (III+VI) content. It had to comply with the following condition $C_3^{Crj} > C_{3p}^{Cr}$

$$w_3(a, b, X) = \sum_{j=1}^d w_3^j(a, b, X) \quad (45)$$

The balance of Cr(III+VI) for both waste streams: the following relation has described the enriched and impoverished one:

$$\sum_{j=1}^d w_3^{uj}(a, b, X) \cdot C_3^{Cnuj} + \sum_{j=d}^k w_3^j(a, b, X) \cdot C_3^{Crj} - w_{3p}(a, b, X) \cdot C_{3p}^{Cr} = 0 \quad (46)$$

The following relation determines the Cr (III+VI) content, in the stream with a higher chromium content:

$$C_3^{Cr} = \frac{\sum_{j=1}^k w_3^j \cdot C_3^{Crj}}{\sum_{j=1}^k w_3^j} \quad (47)$$

A measure of efficiency of dry enrichment was the enrichment degree [35]. This parameter defines the ratio of the contents of Cr(III+VI) before and after dry enrichment, according to the following equation:

$$\epsilon_d = \frac{C_3^{Cr}}{C_{3p}^{Cr}} \quad (48)$$

The general balance of chromic wastes occurring in the process, has been described by the equation:

$$A(a, b, X) - w_2(a, b, X) - w_3(a, b, X) = A^E(a, b, X) \quad (49)$$

In the variants in which the mass of chromium-containing raw material, introduced to node 1 either as chromic mud $w_2(a, b, X)$ or as chromic waste material from the existing heap $w_3(a, b, X)$ is bigger than the mass of chromic mud obtained in process $A(a, b, X)$, the mass of the effective waste $A^E(a, b, X)$ assumes negative values.

Summary and Conclusions

The objective of this work required conducting complex investigations of the chosen chromic wastes (which can be used in the process of obtaining sodium chromate(VI)), in the area determined by the variation range of the selected process parameters. These included the contents of chromium(III+VI) in the charge directed to the calcination ($X(10.5; 19.5)$), the stoichiometric indicator of sodium carbonate ($a(0.2; 1.0)$), and the stoichiometric indicator of calcium oxide ($b(0.5; 1.0)$). The investigation results allowed preparing quantitative description of the desired relations between the fundamental process parameters. The object (process) function, valid in the researched area, was determined, assuming as the base equations of material balance, which describe each of the above-mentioned technological nodes, and using the relations defined on the basis of the experiment results. To elaborate this function it was necessary to create a collection of values characterizing this function and a classification of these values.

Based on the obtained results it is possible to intensify the process of obtaining sodium chromate (VI) in the multivariant system, with the use of chromic waste and to optimize its parameters in terms of environmental protection.

On the basis of the results of the laboratory investigations and analysis of the technical state of the sodium chromate (VI) production process various technological variants of using chromic waste as a substitute for natural raw materials (chromium ore and dolomite) have been worked out. The examination of compositions of chromate charges with different components on the laboratory scale allowed to determine - with the use of statistical methods - the relations of the parameters of the technological process of obtaining sodium chromate (VI) to the selected technological parameters.

The development of different variant ideas of the utilization of chromic waste made it possible to choose the optimal technological solution from among all the variants possible in industrial realization, and to determine the optimal process parameters.

The technology with the use of in process recirculation of the part of the obtained "chromium mud" (variant *Al*) was implemented in "Alwernia" Chemical Works near Cracow in the summer 1999 at new sodium chromate unit. The implementation results showed that the waste quantity per 1 tonne of product were lower at 80%, energy consumption figure at 38% and production cost at 25%, than in the dolomite method. Productivity of Na_2CrO_4 reached 88.5% (20% more than in the dolomite method).

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Appendix Technical Definitions

a	- stoichiometric indicator CaO , [kg/kg]
$A(a, b, X)$	- mass of dry chromic mud formed in the process of obtaining Na_2CrO_4 , [kg]
$A^c(a, b, X) \geq 0$	- mass of chromic mud transported to the storage heaps, [kg]
$A^E(a, b, X)$	- effective waste, the difference between chromic waste that is led out and introduced, [kg]
b	- stoichiometric indicator Na_2CO_3 , [kg/kg]
$\text{CaO}_{(\text{stech})}$	- stoichiometric mass of calcium oxide, [kg]
$\text{Cr}^{Al} \geq 0$	- aluminium content in "i" chromium-containing raw material, [mass % Al_2O_3]
$\text{Cr}^{Ca} \geq 0$	- calcium content in "i" chromium-containing raw material, [mass % CaO]
$\text{C}_A^{\text{Cr}}(a, b, X) \geq 0$	- total Cr content in the chromic mud, [mass % Cr_2O_3]
$\text{Cr}^{\text{Cr}} > 0$	- total Cr(III+VI) content in "i" chromium containing raw material, [mass % Cr_2O_3]
$\text{Cr}^{\text{Cr}} > 0$	- Cr(III) content in the chromium ore, [mass % Cr_2O_3]
$\text{C}_A^{\text{CrCa}}(a, b, X) \geq 0$	- CaCrO_4 content in the chromic mud, [mass % Cr_2O_3]
$\text{Cr}^{\text{CrCa}} \geq 0$	- CaCrO_4 content in "i" chromium-containing raw material, [mass % Cr_2O_3]

$C_A^{Crk} (a, b, X) \geq 0$	- Cr(VI) content in the chromic mud, [mass % Cr ₂ O ₃]	$P(a, b, X)$	- product mass, obtained as water-soluble Na ₂ CrO ₄ , water-soluble, [kg CrO ₃]
$C_i^{CrR} > 0$	- chromium(VI) content in "i" chromium-containing raw material, [mass % Cr ₂ O ₃]	s	- sodium carbonate mass in the charge, [kg]
$C_A^{CrNa} (a, b, X) > 0$	- Na ₂ CrO ₄ content in obtained chromic mud, [mass % Cr ₂ O ₃]	t	- CaO mass in the charge, [kg]
$C_i^{CrNa} > 0$	- Na ₂ CrO ₄ content in "i" chromium-containing raw material, [mass % Cr ₂ O ₃]	$w_i(a, b, X) \geq 0$	- mass of "i" chromium-containing raw material, [kg w _i]
$C_A^{CrR} (a, b, X) \geq 0$	- Cr(III) content in the chromic mud, [mass % Cr ₂ O ₃]	$w_{ik}(a, b, X) > 0$	- mass of "i" raw material, after sintering, [kg]
$C_i^{CrR} > 0$	- chromium(III) content in "i" chromium-containing raw material, [mass % Cr ₂ O ₃]	$w_2(a, b, X)$	- chromic mud mass, returned to the process, [kg]
C_3^{Crj}	- Cr(III+VI) content in "j" fraction, [mass % Cr ₂ O ₃]	$w_3(a, b, X) > 0$	- stream of increased mass Cr(III+VI) content steered to the node 1, [kg]
C_{3p}^{Cr}	- Cr(III+VI) content in the waste prepared to enrichment, [mass % Cr ₂ O ₃]	$w_3(a, b, X)$	- chromic waste mass, introduced from the storing heap to node 2, [kg]
C_3^{Crj}	- decreased Cr(III+VI) content in "j" fraction, [mass % Cr ₂ O ₃]	$w_3^u(a, b, X) > 0$	- mass of the stream with low chromium content, [kg]
C_3^{Crj}	- increased Cr(III+VI) content in the different from "j" fraction, [mass % Cr ₂ O ₃]	$w_{3p}(a, b, X) > 0$	- mass of chromic waste for enrichment process, [kg]
$C_i^{Na} > 0$	- sodium content in "i" chromium-containing raw material, [mass % Na]	$w_3^j(a, b, X) > \delta$	- mass of "j" fraction of defined grain diameters, [kg]
C_i^{Si}	- silica content in "i" chromium-containing raw material, [mass % SiO ₂]	X	- Cr(III+VI) content in the charge, [mass % Cr ₂ O ₃]
d	- divisioning grain diameter, separating impoverished and enriched in Cr(III+VI) fractions, μm]	z	- coefficient of theoretical calculations and experiment consistence
$F(a, b, X) > 0$	- solid phase mass after calcination (sinter), [kg]	$\alpha = 0.01395$	- stoichiometric coefficient, defined from reaction (1), [kg Na ₂ CO ₃ / mass % Cr ₂ O ₃ • 100]
G_p	- mass of substances introduced to the node 1, [kg]	$\beta = 0.023$	- coefficient for recalculating sodium content on sodium carbonate mass, [kg Na ₂ CO ₃ /mass % Na • 100]
G_k	- mass of substances led out from the node 1, [kg]	$\gamma = 0.368$	- coefficient, [kg O ₂ /kg Cr ₂ O ₃]
i	- number of chromium-containing raw material; <i>iutefiwd</i> e (1,-4), i=1 - chromium ore, j=2 - chromic mud from the production, j=3 - chromic wastes from the existing storing heap, j=4 - tannery waste	$\chi = 0.0187$	-stoichiometric coefficient defined from equation (2), [kg CaO /mass % SiO ₂ • 100]
$j > 1$	- number of educed fraction	$\sigma = 0.0224$	- stoichiometric coefficient defined from equation (4), [kg CaO/mass % Al ₂ O ₃ • 100]
k	- number of educed fractions	$\mu = 0.01$	- coefficient recalculating content in mass % on mass fraction, [kg/kg • %]
$m^{CO_2} (a, b, X) > 0$	- mass of educed CO ₂ , [kg]	$\Delta A(a, b, X) > 0$	- change off obtained chromic mud mass, caused by hydration, [kg/kg]
$m^{O_2} (a, b, X) > 0$	- mass of used O ₂ , [kg]	$\Delta F(a, b, X) > 0$	- change of the solid phase mass, [kg]
$m_k^{CaCrO_4} (a, b, X) > 0$	- CaCrO ₄ mass led out from the calcination process, [kg Cr ₂ O ₃]	$\Delta r(a, b, X) > 0$	- change of the solid phase mass, caused by chemical reactions coursing, [kg]
$m_p^{NaCrO_4} (a, b, X) > 0$	- CaCrO ₄ mass introduced with chromium-containing raw materials, [kg Cr ₂ O ₃]	$\Delta wi > 0$	- mass ratio of the mass change during calcination of "i" chromium-containing raw material, [kg/kg w _i]
$m_k^{Na_2CrO_4} (a, b, X) > 0$	- Na ₂ CrO ₄ mass led out from calcination process, [kg Cr ₂ O ₃]	$\varphi = 0.415$	- stoichiometric coefficient, [kg]
$m_p^{Na_2CrO_4} (a, b, X) > 0$	- Na ₂ CrO ₄ mass introduced with chromium-containing raw materials, [kg Cr ₂ O ₃]	$\kappa = 0.76$	- recalculating coefficient, [kg Cr ₂ O ₃ /kg CrO ₃]
n	- number of chromium-containing raw materials	$\varphi = 1.62$	- recalculating coefficient, [kg Na ₂ CrO ₄ /kg CrO ₃]
$Na_2CO_{3(stech)}$	- sodium carbonate stoichiometric mass, result of equation (1), [kg]	ηd	- separation degree, [kg/kg]
		ϵd	- enrichment degree, [mass % Cr _j Cymass % Cr ₂ O ₃]