

The Effect of Chromic Mud Graining on the Technological Parameters of the Sodium Chromate Production Process

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Abstract

The most important solution in the new sodium chromate production process implemented in Alwernia Chemical Works is in-process recycling of chromic mud. This allows lessening the hazard to the natural environment resulting from released chromic waste. It also involves economical advantages. This paper presents studies on the optimisation of this process using of a fuzzy logic method. The influence of the grain size of chromic mud on the sodium chromate production process with chromic mud in process recycling has been estimated. The optimal values of the process parameters can be achieved applying preliminary ground chromic mud and fine-ground fractions of chromic ore. "Deep" milling of chromic mud is not necessary.

Keywords: sodium chromate, chromic mud, in-process recycling, optimisation.

Introduction

Chromium is more abundant than cadmium, cobalt, copper, lead, molybdenum, nickel, or zinc. Their compounds are highly varied and widely distributed in the occupational, domestic, and recreational environment. Chromium has been identified both as an essential micronutrient and as a chemical carcinogen. The essentiality or carcinogenicity of chromium is a function of its chemical form [1].

Chemical compounds of chromium are made from sodium chromate, a basic intermediate product for the production of all other chromium compounds. At present, the world's production capacity rate of sodium chromate is about 600,000 tons per year. Chrome chemicals do not instantly spring to mind as the most exciting sector of the

chemical industry, but their useful properties make them indispensable in end uses as diverse as leather tanning, timber preservation, metal coating and alloying, and pigments. Today, over 70 chromium compounds are in commercial use. However, only a few of these compounds are produced in large quantities, notably sodium chromate and dichromate, potassium chromate and dichromate, chromic acid, chromic oxide and basic chromic sulphate [2-6].

The basic environmental problem of the chromium compound production was a large quantity of produced waste - up to 4,000 kg/t of sodium chromate [7-9]. The use of the chromium compounds in many industries was also a source of a large quantity of waste e.g. leather waste after chrome tanning and solid waste containing chromium hydroxide after chromic wastewater treatment as well as a large amount of liquid waste, especially from tanneries are disposed or released [10-12]. Another major defect of the

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dolomite method was low process efficiency in relation to the chromium that was obtained (about 69%) and high consumption of primary or secondary raw materials.

The only Polish producer of chromium compounds is Alwernia Chemical Works near Kraków. Approximately 2.5 million tons of waste have been collected over the 50 years of production of chromium compounds in Alwernia. Until 1999 about 80% of this chromic waste was obtained in sodium chromate production with the use of a classic dolomite method [4-6,10-16].

The new sodium chromate technology implemented in 1999 in Alwernia allowed substituting about 50% of natural raw materials with recycled chromic waste from sodium chromate production (so-called chromic mud) [6-17].

The aim of this research was to determine dependence of grain size of chromic mud and basic process parameters of the sodium chromate production with chromic mud recycling. Raw material consumption, the quantity of produced waste, and process efficiency were considered basic process parameters.

Material and Methods

Sodium Chromate Technology

Figure 1 presents a flow sheet of the sodium chromate process with in-process chromic mud recycling, implemented into industrial practice in 1999. In this process a dolomite filler was replaced with recycled chromic mud with a little addition of calcium oxide [12-19]. This allowed the amount of disposed chromic mud to be reduced by almost 80% and increased the yield of the process from 69% to 88% (in relation to chromium). In consequence, the consumption of raw materials and energy was significantly reduced. The implementation of the new technology of sodium chromate production resulted in the character of this production changing from high waste to

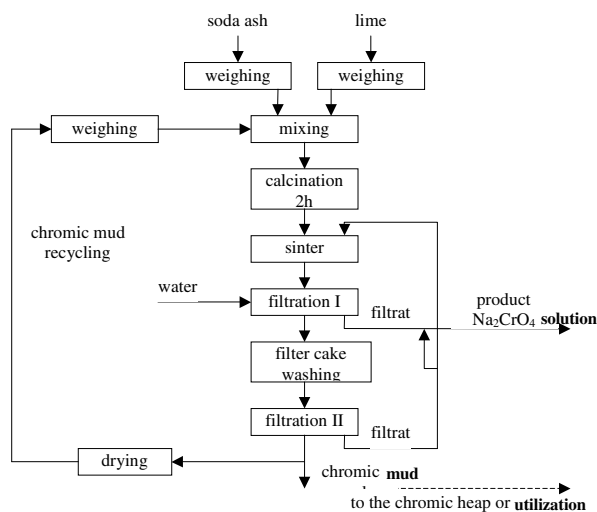


Fig. 1. Flow sheet of the sodium chromate production process with the use of chromic mud in-process recycling.

low waste. In connection with the modernisation of the equipment and computerisation of technological processes, the installation of modern dust collectors resulted in the creation of a whole complex of chromium production plants at a very good technical level [13,15,19].

Raw materials used as the chromate charge component are chromic ore, chromic mud, soda ash and lime. The mixture is calcined in the rotary kiln at temperatures of 1423-1473K in an oxidising atmosphere. The produced sinter is leached in water. During leaching Na_2CrO_4 is dissolved in water and the obtained suspension is filtrated. The filtrate (Na_2CrO_4 solution) is a product. The filter cake (chromic mud) is pulped with water and filtrated once more. The product from the second filtration is reused in the leaching process.

The oxidation of Cr(III) to Cr(VI) is essential in the production process of Na_2CrO_4 . During the calcining process, both sodium carbonate and sodium chromate(VI) exist as a liquid phase as bicomponent eutectic systems, i.e. $\text{Na}_2\text{CrO}_4 - \text{Na}_2\text{CO}_3$ and $\text{Na}_2\text{CrO}_4 - \text{Na}_2\text{SiO}_3$. Hence, air diffusion in the system is constrained and the oxidation reaction is slowed [7-12]. The use of a finely ground filler increases the surface of the solid phase and decreases the thickness of the melted layers on the grains.

In this work the influence of grain size of chromic mud on some technological parameters of sodium chromate production process was estimated. These parameters are:

- raw material consumption (chromic ore, sodium carbonate, chromic mud and calcium oxide),
- process efficiency related to Cr content (total in the charge or from chromic ore only),
- productivity of the process defining the quantity of the Na_2CrO_4 solution produced from the charge unit introduced into the process,

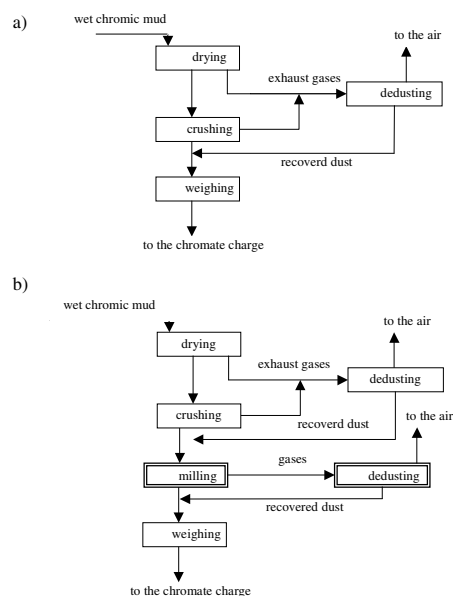


Fig. 2. Flow sheet of the preparation of chromic mud used as a component of the chromate charge; a - implemented solution, b - new solution (= modernised or new units).

- quantity of chromic mud produced in the process,
- quantity of the effective waste, the difference between output and input of chromic waste.

The evaluation of optimal grain size of dried chromic mud is very important for future technical solution of the sodium chromate production process. Actually, recycled chromic mud is prepared before being used as a component of the chromate charge according to a flow sheet presented in Figure 2a. It is dried in a rotary dryer and only crushed in a hammer mill to a grain size <1mm. The gases from the hammer mill are incorporated into the stream of exhaust gases from the dryer. This stream is dedusted with the use of a bag filter. The question arises whether the initial crushing of the dried chromic mud could guarantee high efficiency of chromium recovery from the chromic mud. The problem is important because as an alternative the milling of the dried chromic mud with ball mill to obtain grain size below 90 μm (Figure 2b) was discussed.

To implement the solution presented in Figure 2b the existing raw material ball mill should be modernised and a new dedusting unit of the chromic mud mills and a rather complicated transport path should be built. The investment cost was estimated at ~1.5 million USD for such a new unit. The results of our research could help to determine whether or not this investment is really necessary.

Experimental

The laboratory research was carried out in conditions that enabled simulation of industrial Na_2CrO_4 production with chromic mud recycling. The basic stages of the process, the charge preparation, calcining of charge, sinter leaching and filtration, were realised.

The following raw materials were applied: chromic ore from Kazakhstan containing 48.52% Cr_2O_3 ; chromic mud from the current production of "Alwernia" Chemical Works (containing [%]: Cr_2O_3 - 7.47, Fe_2O_3 - 11.59, Al_2O_3 - 12.24, CaO - 25.61, MgO - 25.47 and SiO_2 - 6.61); calcium oxide (after calcination at 1023 K during 2hrs); soda ash of analytical grade. For preparation of the chromate charge six fractions of chromic ore and chromic mud were used. These fractions were obtained by classification with vibrating screens. Their characteristics are presented in Table 1.

Chemical analysis, X-ray powder diffraction and thermogravimetric methods were used to analyse the chemical and phase compositions for all applied fractions [20]. The raw material mixtures were composed with the following assumption: Cr_2O_3 content in the charge $X = 14.7\%$, coefficient of Na_2CO_3 stoichiometry $a = 0.75$ and coefficient of CaO stoichiometry $b = 0.88$. The quantity of chromic ore, sodium carbonate, calcium oxide, and chromic mud used was determined by the method given in works [17,18,20,21].

The laboratory tests were realised as follows: 25 g of reagent mixtures was calcined for 2h at 1423K in a porcelain crucible in a chamber furnace. Sinters, after

Table 1. Characteristics of chromic ore and chromic mud fractions.

Chromic ore		
Number	Grain size [mm]	Chromium content [% Cr_2O_3]
R1	0.09 - 0.1	51.61
R2	0.08 - 0.09	52.32
R3	0.072 - 0.08	52.34
R4	0.063 - 0.072	52.32
R5	0.05 - 0.063	52.65
R6	< 0.05	47.73
Chromic mud		
Number	Grain size [mm]	Chromium content [% Cr_2O_3]
B1	0.09 - 0.1	7.91
B2	0.08 - 0.09	7.75
B3	0.072 - 0.08	7.35
B4	0.063 - 0.072	6.56
B5	0.05 - 0.063	7.21
B6	< 0.05	5.45

cooling and crushing, were extracted with water (80 cm^3) at 353K for 1.5h. The suspension was agitated (magnetic stirrer). Next, the obtained slurry was separated in a vacuum filter. The last step was the washing of the filter cake with water (50 cm^3) at 353K. The solution (filtrate) and sludge were analysed to estimate different types of chromium compound contents (total chromium - Cr(III) and Cr(VI) compounds, water- and acid soluble Cr(VI) compounds). Filtrate and sludge amount (mass, volume) and sludge moisture were determined to calculate the quantity of the product expressed as 67.5 percentage water solution of Na_2CrO_4 .

On the basis of the investigation results, the basic parameters of the sodium chromate production process were calculated. The fuzzy logic system [20,22,23] was used to find the optimal composition of charge used in the Na_2CrO_4 production process. The estimation of the process parameters was made by the matrix method in which Leopold's causal-effect matrix was used. This matrix is designed as a grid of rows and columns where conducted laboratory attempts (sample numbers) are given in rows, and the Na_2CrO_4 process parameters in columns. According to the chosen criteria, the values of the characteristic process parameters were located in a common cell. The accepted values are denoted by "+", not accepted by "-" and admissible by "+/-". The tests for which one or more parameters values were determined as not acceptable were discarded. The test for which all or the majority of values of all parameters were determined as acceptable was considered an optimal composition of the chromate charge.

Results

These investigations determined the effect of the chromic mud graining on the sodium chromate production process. Table 2 shows the results of the laboratory tests (characteristics of filtrate – product and leach residue – waste) and the calculated amount of product (67.5% solution of Na_2CrO_4). These results allowed to calculate basic process parameters graphically presented in Figures 3-5.

The minimum of chromic ore consumption (920 – 940 kg / 1t of the product) was observed for B2 and B3 chromic mud fractions. The maximum of lime consumption (360 – 370 kg / 1t of the product) was found when B4 and B6 fractions of chromic mud were used. The maximum value of soda ash consumption (about 675 kg / 1t of the product) was found for B4 fraction of chromic mud. The differences of the minimum and maximum values of raw material consumption varied by about 10%.

Table 2. Results of laboratory test of sodium chromate production with the use of different fractions of the chromic mud.

Sample	Filtrate			Filter cake					Quantity of product (contained 67.5% Na_2CrO_4) [g]
	Mass [g]	Volume [cm ³]	Chromium content [% Cr_2O_3]	Mass [g]	Chromium content [% Cr_2O_3]			Moisture [%]	
					Total	Water soluble	Acid soluble		
B1R1	99.1	95	23.81	19.0	5.51	0.48	3.28	26	4.41
B1R2	100.1	96	24.06	17.9	5.24	0.37	3.11	24	4.60
B1R3	100.6	97	25.58	18.1	5.33	0.55	3.38	24	4.69
B1R4	98.4	95	24.32	18.8	4.80	0.52	2.70	28	5.78
B1R5	100.4	96	23.56	17.9	4.34	0.55	2.36	26	5.74
B1R6	98.7	95	25.58	19.5	4.34	0.49	3.21	31	6.08
B2R1	101.4	98	24.06	17.4	4.97	0.51	2.87	23	4.50
B2R2	99.4	95	25.08	19.2	4.70	0.37	2.57	29	4.64
B2R3	100.2	96	24.82	18.3	4.80	0.44	2.60	27	5.95
B2R4	100.8	96	23.56	17.6	4.43	0.54	2.50	24	5.69
B2R5	100.4	96	23.81	17.4	4.07	0.58	2.23	23	5.76
B2R6	98.2	94	25.33	20.6	4.16	0.41	3.01	34	6.02
B3R1	126.1	123	23.30	22.8	4.70	0.23	2.80	25	4.38
B3R2	127.2	125	24.82	22.1	4.78	0.29	2.77	22	4.65
B3R3	127.6	124	24.32	22.0	4.88	0.47	2.77	21	5.93
B3R4	125.2	123	24.06	24.0	4.98	0.41	3.24	27	4.55
B3R5	125.2	122	24.06	23.9	4.80	0.30	3.11	27	5.82
B3R6	126.8	124	25.33	23.3	4.88	0.50	3.68	25	6.07
B4R1	100.9	97	25.33	18.1	5.25	0.43	3.14	23	4.67
B4R6	99.9	96	25.33	18.7	4.43	0.57	3.21	27	6.07
B5R1	127.1	125	25.58	21.4	4.79	0.15	3.07	23	4.79
B5R2	127.7	125	25.33	20.5	4.52	0.46	2.80	21	4.74
B5R3	127.8	124	24.06	20.4	3.89	0.09	2.67	22	5.82
B5R4	127.2	124	25.33	21.0	3.98	0.39	2.74	23	4.72
B5R5	127.8	125	24.06	20.5	3.53	0.50	2.47	22	5.86
B5R6	127.1	124	25.33	21.9	3.98	0.55	3.11	26	5.97
B6R1	124.9	122	25.58	22.8	4.25	0.10	3.01	29	4.74
B6R2	125.5	122	25.84	23.0	4.43	0.11	3.28	29	4.81
B6R3	126.2	123	23.81	21.9	4.34	0.35	3.07	27	5.71
B6R4	126.2	123	22.80	22.1	4.25	0.11	3.21	27	5.55
B6R5	123.3	121	23.81	24.4	4.43	0.15	3.51	32	5.76
B6R6	123.8	121	25.58	24.5	3.98	0.13	3.55	34	6.03

The maximum of chromic mud consumption (~2,950 kg/1t of the product) occurs for B3 chromic mud fraction. The differences of these parameter values ranged by about 10%. The maximum of effective waste quantity (500 - 520 kg / 1t of the product) occurs for B2, B3 and B4 chromic mud fractions, the minimum of these parameters – for the finest fractions of chromic raw materials (at the limitations of the examined area). The differences of the minimum and maximum values of the effective waste quantity are very high.

The highest values of process efficiency (related to the Cr content in the chromic ore only) (~105%) are observed

for B2 and B3 chromic mud fractions. The efficiency values for B3 chromic mud fraction are insignificantly lower. The lowest values of Na₂CrO₄ production process efficiency, which is expressed in relation to total chromium concentration in the chromate charge, varied from 73 to 75%, were observed in the chromic ore for B3 and B4 chromic mud fractions. The differences of the minimum and maximum of this parameter ranged by about 8%. The minimum of productivity (lower than 0.225 kg of product / 1 kg of charge) was seen for B3 chromic mud fraction.

The above analysis allowed us to discover that the use

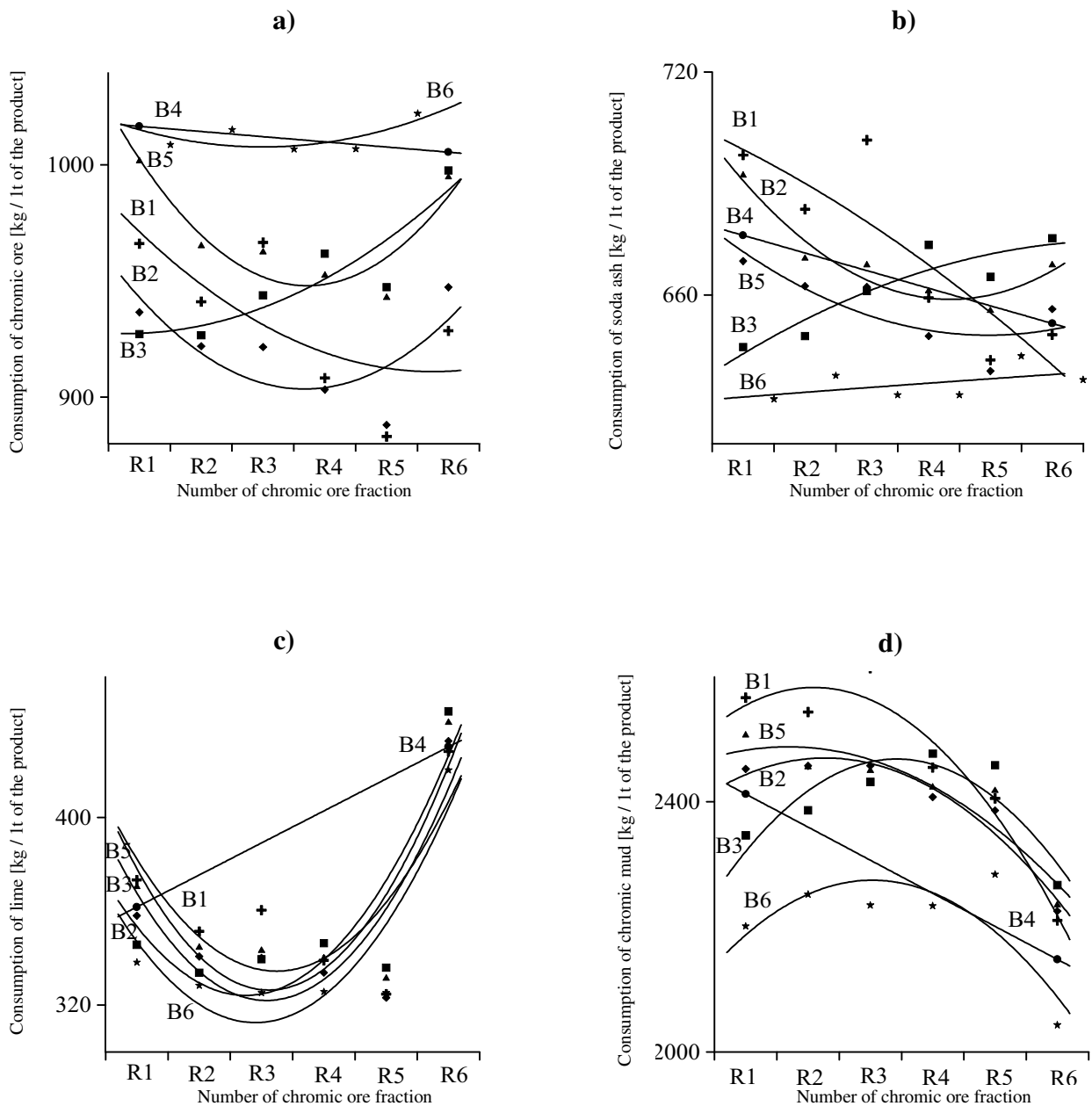


Fig. 3. Dependence of consumption of: a – chromic ore, b – soda ash, c – lime, d – chromic mud, and grain size of the chromic ore (B1-B6 used symbols of the chromic mud fractions according to Table 1).

Table 3. Estimation criteria of the parameters of sodium chromate production process.

Estimation criteria	Raw material consumption[kg / 1t of product]				Waste quantity [kg / 1t of product]		Process efficiency related to the chromium [%]		Productivity [kg / 1kg of the charge]
	chromic ore	chromic mud	soda ash	lime	produced in the process	effective waste	in chromic ore	in chromic ore and waste	
accepted +	<950	<2300	<650	<330	<2700	<400	>105	>80	>0.240
admissible +/-	950 - 1000	2300 - 2420	650 - 665	330 - 345	2700 - 2850	400 - 500	100 - 105	77 - 80	0.235 - 0.240
not accepted -	>1000	>2420	>665	>345	>2850	>500	<100	<77	<0.235

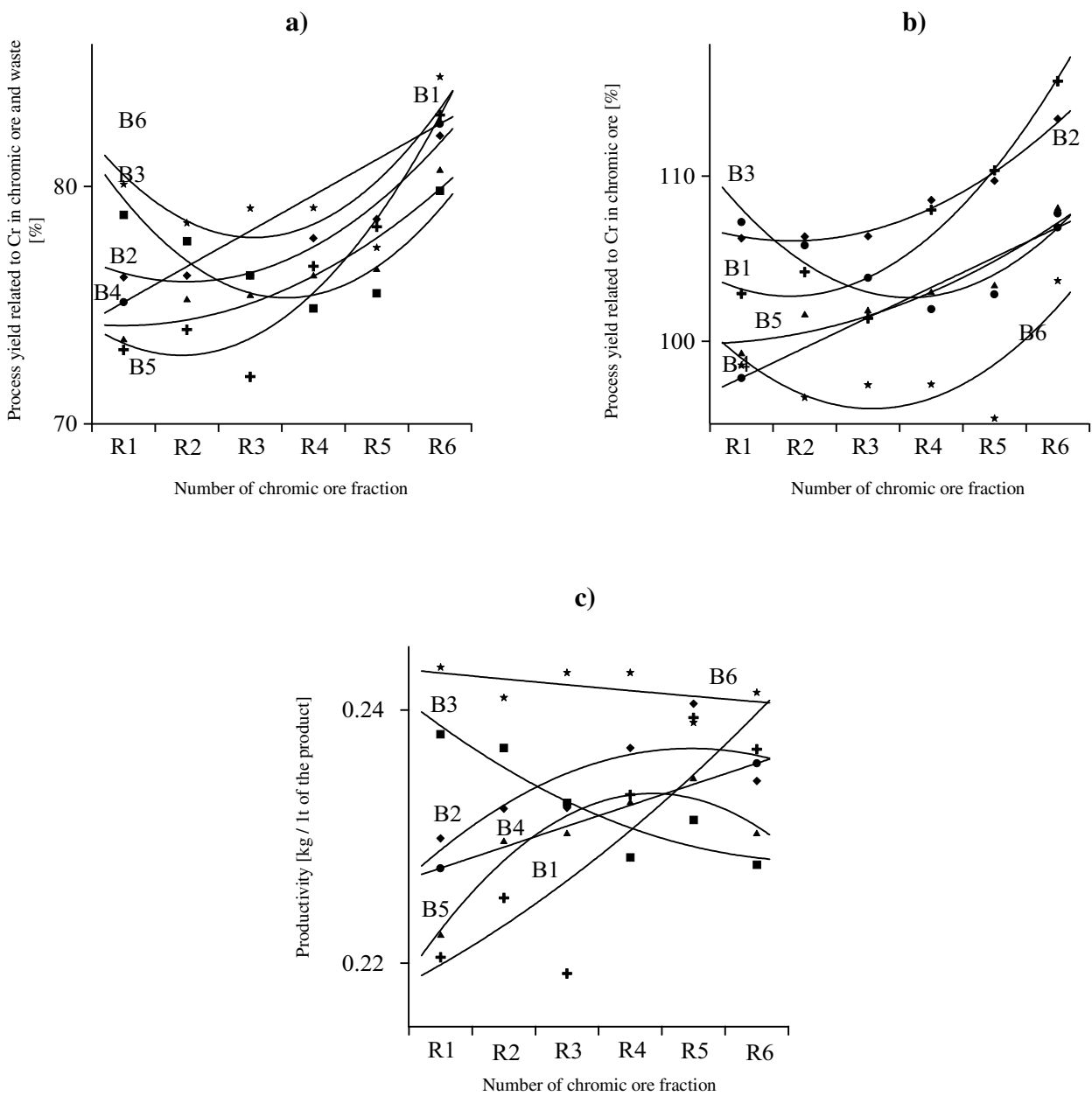


Fig. 4. Dependence of the sodium chromate process efficiency in relation to: a – chromium content in the chromate charge, b – chromium content in the chromic ore and c – dependence of the productivity coefficient, and grain size of the chromic ore (B1-B6 used symbols of the chromic mud fractions according to Table 1).

Table 4. Process parameters of Na₂CrO₄ production with the use of different chromic mud and chromic ore fractions.

Sample	Raw material consumption[kg / lt of product]				Waste quantity [kg / lt of product]		Process efficiency related to the chromium [%]		Productivity [kg / 1kg of the charge]
	chromic ore	chromic mud	soda ash	lime	produced in the process	effective waste	in chromic ore	in chromic ore and waste	
R1B1	966 +/-	2566 -	698 -	373 -	3114 -	548 -	103 +/-	73 -	0.220 -
R1B2	937 +	2453 -	669 -	358 -	2924 -	471 +/-	106 +	76 -	0.230 -
R1B3	927 +	2346 +/-	646 +	346 -	2833 +/-	486 +/-	107 +	79 +/-	0.238 +/-
R1B4	1017 -	2412 +/-	676 -	362 -	2991 -	579 -	98 -	75 -	0.228 -
R1B5	1002 -	2506 -	692 -	370 -	2940 -	433 +/-	99 -	74 -	0.222 -
R1B6	1009 -	2201 +	632 +	338 +/-	2608 +	408 +/-	98 -	80 +	0.243 +
R2B1	941 +	2544 -	683 -	351 -	3027 -	483 +/-	104 +/-	74 -	0.225 -
R2B2	922 +	2458 -	662 +/-	341 +/-	2851 -	394 +	106 +	76 -	0.232 -
R2B3	927 +	2386 +/-	649 +	334 +/-	2852 -	466 +/-	106 +	78 +/-	0.237 +/-
R2B5	965 +/-	2456 -	670 -	345 +/-	2828 +/-	372 +	102 +/-	75 -	0.230 -
R2B6	1015 -	2252 +	638 +	328 +	2654 +	403 +/-	97 -	79 +/-	0.241 +
R3B1	967 +/-	2614 -	702 -	360 -	3137 -	525 -	101 +/-	72 -	0.219 -
R3B2	922 +	2458 -	662 +/-	340 +/-	2859 -	401 +/-	106 +	76 -	0.232 -
R3B3	944 +	2432 -	661 +/-	340 +/-	2909 -	477 +/-	104 +/-	76 -	0.233 -
R3B5	963 +/-	2450 -	668 -	343 +/-	2784 +/-	334 +	102 +/-	75 -	0.230 -
R3B6	1007 -	2234 +	633 +	325 +	2593 +	359 +	97 -	79 +/-	0.243 +
R4B1	908 +	2455 -	659 +/-	339 +/-	2846 +/-	391 +	108 +	77 -	0.233 -
R4B2	903 +	2408 +/-	649 +	334 +/-	2772 +/-	365 +	109 +	78 +/-	0.237 +/-
R4B3	962 +/-	2477 -	673 -	346 -	3018 -	541 -	102 +/-	75 -	0.228 -
R4B5	952 +/-	2423 -	661 +/-	340 +/-	2751 +/-	328 +	103 +/-	76 -	0.233 -
R4B6	1007 -	2234 +	633 +	326 +	2613 +	380 +	97 -	79 +/-	0.243 +
R5B1	883 +	2405 +/-	643 +	325 +	2732 +/-	327 +	110 +	78 +/-	0.239 +/-
R5B2	888 +	2386 +/-	640 +	323 +	2701 +/-	315 +	110 +	79 +/-	0.240 +
R5B3	947 +	2459 +/-	665 +/-	336 +/-	2954 -	495 +/-	103 +/-	76 -	0.231 -
R5B5	943 +	2418 +/-	656 +/-	331 +/-	2679 +	262 +	103 +/-	77 -	0.235 +/-
R5B6	1022 -	2284 +	644 +	325 +	2725 +/-	441 +/-	95 -	77 -	0.239 +/-
R6B1	929 +	2210 +	649 +	428 -	2826 +/-	616 -	116 +	83 +	0.237 +/-
R6B2	947 +	2225 +	656 +/-	433 -	2833 +/-	608 -	114 +	82 +	0.234 -
R6B3	998 +/-	2267 +	675 -	445 -	3033 -	766 -	108 +	80 +	0.228 -
R6B4	1006 -	2148 +	652 +/-	430 -	2831 +/-	683 -	107 +	83 +	0.236 +/-
R6B5	995 +/-	2235 +	668 -	441 -	2780 +/-	545 -	108 +	81 +	0.230 -
R6B6	1037 -	2043 +	637 +	420 -	2686 +	643 -	104 +/-	85 +	0.241 +

of the coarse ground dried chromic mud (B2 and B3 fractions) is sufficient to reach the most advantageous values of the analysed Na₂CrO₄ production process parameters.

The obtained results cannot be directly used to determine the optimal composition of the chromate charge due to a high number of analyzed figures. For this reason the simplified Leopold's matrix was used to select the optimal composition of the chromate charge. The choice

was made according to the criteria presented in Table 3. The calculated process parameters and optimisation results are given in Table 4.

On the basis of the above selection results it can be seen that the satisfactory values of the process parameters were obtained for samples denoted by B1R5, B2R5 and B2R4. These charges contained chromic mud with grain size >0.08 mm and chromic ore with grain size 0.05 – 0.072 mm. Thus, preliminary grinding of chromic mud and the

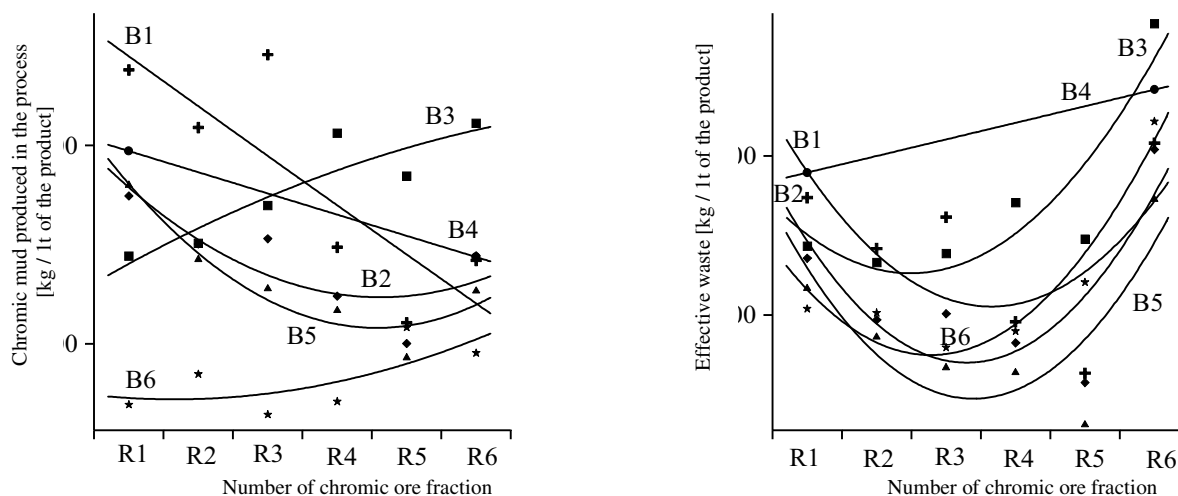


Fig. 5. Dependence of quantity of: a – chromic mud produced in the process, b – effective waste, and grain size of the chromic ore (B1-B6 symbols of the chromic mud fractions according to Table 1).

currently used milling of chromic ore with ball mills is advantageous for the sodium chromate obtaining process.

Moreover, it appears that practically the chosen fractions have the same chromium content as others, but in fact this is not as important a factor as the interfacial surface of the reagents.

Conclusions

The investigation results show that the Na_2CrO_4 production process depends on the comminution of raw materials. The optimal values of the process parameters can be achieved when preliminary ground chromic mud and fine-ground fractions of chromic ore are used. “Deep” milling of chromic mud is not necessary.

The use of optimal fractions of chromic raw materials resulted in an increase in process efficiency and productivity and a decrease in the quantity of produced waste and used raw materials.

Optimisation of the results of laboratory tests made with the fuzzy logic method allowed us to find the best chromate charge from the 32 tested. It was a B2R5 sample which had the following raw material consumption [kg / 1t of the product]: chromic ore – 888; soda ash – 639.5; calcium oxide – 323.1; chromic mud - 2386. The quantity of the effective waste was 314.8 kg and process efficiency in relation to total chromium contained in the chromate charge was 78.6%.

These results prompted us to suggest to Alwernia Chemical Works that an investment in a new milling unit of chromic mud is not necessary.

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