

Chemical Science International Journal

30(8): 13-24, 2021; Article no.CSIJ.75155 ISSN: 2456-706X (Past name: American Chemical Science Journal, Past ISSN: 2249-0205)

Obtaining Caustic Soda and Burkeite by Caustification of Mixture of Corbonate and Sodium Sulphate

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/CSJI/2021/v30i830245 *Editor(s):* (1) Prof. Akmal S. Gaballa, Zagazig University, Egypt. *Reviewers:* (1) Sri Adelila Sari., Universitas Negeri Medan, Indonesia. (2) Khushal Kapadiya, RK University, India. Complete Peer review History: https://www.sdiarticle4.com/review-history/75155

Original Research Article

Received 02 August2021 Accepted 11 October 2021 Published 16 October 2021

ABSTRACT

The optimal technological parameters for the production of caustic soda from sodium carbonate and sulfate and calcium hydroxide have been established. The influence of the concentration of lime milk on the rate of filtration by sediment and filtrate has been studied.

Purpose of the Work: The purpose of this work is to determine the physicochemical basis for the production of sodium hydroxide and burkeite by causticization of sodium carbonate and sulfate.

Scientific Novelty: In comparison with the known works, a theoretical profoanalytical analysis of the one-cation of four-component system $Na^+,OH^-, CO_3^{2-}, SO_4^{2-}$ and its constituents was carried out for the first time, and also determined the optimal technological parameters of causticization of solutions for local carbonates and sodium sulfates.

Features of the Work:

- the influence of the main technological parameters on the processes of causticization, filtration, evaporation;

- research of intermediate and finished products by modern physicochemical methods;

- study of the rheological properties of the solution depending on the temperature and concentration of the resulting solutions.

Keywords: Soda ash; mirabilite; lime milk; sodium hydroxide; temperature; ratio; residue; filtration; density; viscosity; sediment; reaction; crystal.

1. INTRODUCTION

It is known [1,2] that when caustic soda is obtained by causticization, to prevent the formation of personite $Na_2CO_3 \cdot CaCO_3 \cdot 2H_2O$, weak liquors are obtained containing about 130g/lNaOH,30 g/lNa₂CO₃ and 11,3 g/lNa₂SO₄.

In the further process of evaporation of the causticizing solution, it is important not only to maximally isolate impurities into the solid phase, but also to obtain large rapidly precipitating crystals of Na_2CO_3 , Na_2SO_4 and Na_2CO_3 . $2Na₂SO₄$, for which it is necessary to maintain the ratio

 $Na₂SO₄: Na₂CO₃$ at least 0.5 [3]. Therefore, before feeding to the evaporation to achieve this ratio in the clarified weak liquor, it is customary to add a lack of sodium sulfate [4].

2. METHODOLOGY

Thesystems $Na_2CO_3 - Na_2SO_4 - H_2O$; $Na_2CO_3 NaOH - H₂O$; $Na₂SO₄ - NaOH - H₂O$ have been studied by the isothermal solubility method at temperatures 25, 50, 75 and 100 \degree C. The crystallization fields of $Na₂SO₄$. $2H_2O$, $Na_2SO_4, Na_2CO_3 \cdot 7H_2O, Na_2CO_3 \cdot H_2O$ and double salt $2Na_2SO_4 \cdot Na_2CO_3$ are differentiated. Microscopic and qualitative X-ray phase analysis of the obtained products was carried out. After equilibrium was established, samples of the liquid and solid phases were taken for analysis and determination of the location of the figurative point of the system. The samples were analyzed for the content of sulfate, carbon oxides, sodium and calcium.

The initial components, evaporated liquid phase and the dried sediment have been analyzed for the content of $Na^+, OH^-, CO_3^{2-}, SO_4^2$ ions according to well-known methods [4-5].

We have previously shown [3-5] that when causticizing soda ash in the presence of natural mirabilite at various ratios of $Na₂CO₃: Na₂SO₄$, weak solutions are formed containing $NaOH$, $Na₂CO₃$, $Na₂SO₄$.

To determine the method of processing this solution, a theoretical graphic-analytical analysis of one-cation four-component system $Na^{+}//$

 OH^- , 1/2 CO_3^{2-} , 1/2 $SO_4^{2-} - H_2O$ and its components $Na^{+}//OH^{-}$, 1/2 $CO_3^{2-} - H_2O$; $Na^{+}//$ OH^- , 1/2 $SO_4^{2-} - H_2O$; $Na^+//SO_4^{2-} - H_2O$ have been carried out. (Fig. 1, Table 1) [6,7]. In this case, two options for processing this solution have been established:

-when the ratio Na_2CO_3 : $Na_2SO_4 = 1:0$ – 0.5: 0.5 with obtaining in the stage of causticization a weak solution of the composition (wt.%): $NaOH - 9.5$; $Na_2SO_4 - 6.10$; $Na_2CO_3 -$ 6.0. After evaporation of such a solution, burkeite and caustic soda with a concentration of at least 30% can be obtained.

-when the ratio Na_2CO_3 : $Na_2SO_4 = 0.2$: 0.8 – 0: 1 to obtain at the stage of causticization a weak solution of the composition (wt.%): $Na₂SO₄$ – 8,2; $Na_2CO_3 - 6.0$. After evaporation, purified sodium sulfate and a significant amount of concentrated $NaOH$ can be obtained. However, this process is energy-intensive and low-tech, and therefore it is advisable to carry out the vaporization with the addition of the calculated amount of soda ash. When the degree of evaporation is not more than 60%, burkeite precipitates, after the separation of which the mother solution returns to the beginning of the process.

3. RESEARCH RESULTS

Studies [4,7,8] have shown that during causticization of soda ash and sodium sulfate, depending on the ratio of the initial components and the process temperature, solutions of $NaOH$, $Na₂CO₃$, $Na₂SO₄$ are formed, practically free of calcium and magnesium ions.

The results of experiments and analysis of the four-component system $NaOH - Na_2CO_3 Na₂SO₄ - H₂O$ showed that the evaporation of the resulting solution also forms $Na₂CO₃$. $2Na₂SO₄$ - burkeite.

Therefore, from soda ash and natural low-quality mirabilite, it is possible to simultaneously obtain a solution of sodium hydroxide and burkeite. Therefore, in the future, the process of causticization of a solution of calcined soda with lime milk in the presence of mirabilite has been studied. In the experiments, the mass ratio of $Na₂CO₃$: $Na₂SO₄$, the norm, the concentration of lime milk, the rate of clarification and filtration of the suspension have been determined. The liquid and solid phases were analyzed for the content of Na^+ , Ca^{2+} , Mg^{2+} , OH^- , CO_3^{2-} , SO_4^{2-} ions by wellknown methods [9-10].

The content of OH^- , CO_3^{2-} , SO_4^{2-} ions, depending on the stoichiometric norm of $Ca(OH)$ and the ratio of $Na_2CO_3 \tcdot 2Na_2SO_4$,, ranges from 0.33-3.49; 0-10.7 and 0.11-2.62% respectively. The kinetics of the process (Fig. 1) of settling is characterized by clarification for 5 hours at a ratio of Na_2CO_3 : $Na_2SO_4 = 1:0$. In this case, the degree of clarification reaches only 60% by the formation of a turbid liquid phase, and the thickened part is not clearly separated. With an increase in the proportion of sodium sulfate to

the ratio $Na_2CO_3 \cdot 2Na_2SO_4 = 0.5:0.5$, the transparency of the liquid phase increases with the proportion of the condensed part of 40-45%. A further increase in this ratio leads to a reduced proportion of the thickened part to 5-10% within 5 hours.

When causticizing, the ratio of Liquid:Solid (L:S) in the system fluctuates in the range (9-1.39): 1, and the filtration rate does not exceed 40-120 kg / m2h. One of the reasons for the low filtration rate is the high (L:S)value and the content of particles with different diameters, from which small particles are precipitated at much lower rates.

The L:S ratio of the suspension has a great influence on the filtration rate. In the experiments, the suspension ratio L:S and the temperature varied within 2-13: 1 and 30- 90°C, respectively.

The filtration rate in the causticization process without using a circulating solution ranges from 119-411 kg/m²·h with a ratio of Na_2CO_3 : $Na_2SO_4 = 1$: 0in the intervals L:S - (2-13): 1.

With an increase in the content of Na_2SO_4 , in the system, the sediment gradually loses its friability (Fig. 2, a and b) and turns into an adhesive mass (c, d), which significantly reduces the rate of the filtration process. The average crystal size of the sediment is 3.63 microns.

Fig. 1. Kinetics of suspension clarification. Norm of $Ca(OH)_{2}$ **-100%**

Fig. 2. Microscopic images of samples: a) sludge; b) sediment during evaporation

Table 1. Influence of technological parameters on the filtration rate of the pulp

With the ratio Na_2CO_3 : $Na_2SO_4 = 0.8$: 0.2 when using a circulating solution in the causticization process, the filtration rate is 25 - 82 kg / m2h higher than with the ratio Na_2CO_3 : $Na_2SO_4 = 1:0$. However, at L:S = 13: 1 it is 19kg/m²h lower. It should be noted that with the ratio $Na₂CO₃$. $2Na_2SO_4 = 0.5: 0.5$, the filtration rate is almost 2-4 times lower than with the ratios 1: 0; 0.8:0.2 in the interval $L: S = 2-13:1$.

In order to increase the $NaOH$ content to 8.2% in a weak lye, the causticization process has been carried out with a circulating solution with a concentration of 3.7 and 11% $NaOH$. With a ratio of Na_2CO_3 : $Na_2SO_4 = 1:0$ and 0.8:0.2 and a concentration of a circulating solution of 3 and 7% NaOH within 20 hours, the degree of clarification reaches 80, 60, 70 and 30%, respectively, and when the ratio ratio $Na₂CO₃$. $Na_2SO_4 = 0.5: 0.5$ does not exceed 30 and 20% (Fig. 3).

At a later date, we studied the process of evaporation of weak solutions formed during the causticization of sulfate-carbonate-sodium solutions with the ratio Na_2CO_3 : Na_2SO_4 = 1.0; 0.8: 0.2; 0.5: 0.5. To carry out the stripping process, weak solutions were prepared with the indicated ratios of the components obtained by causticizing soda ash at a temperature of 95°C, a rate of 18% lime milk 100%, a process duration of 2 hours and atmospheric pressure. After reaching the given degree of evaporation, the suspension was filtered to separate the precipitated crystals.

The content of ions in a weak solution (wt%): $Na^+ - 6.11$; 4.17; $Ca^{2+} 0.04; 0.02; 1.02; 0H^- - 2.71; 1.91; 1.13; CO_3^{2-} -$ 2.12; 0.58; 0.59; respectively, with the ratio Na_2CO_3 : $Na_2SO_4 = 1.0$; 0.8: 0.2; 0.5: 0.5.

Experimental data (Table 4) showed that with a decrease in the ratio $Na₂CO₃$: $Na₂SO₄$ from 1:0 to 0.5:0.5 and an increase in the degree of evaporation from 60 to 80%, a solid phase is formed, the amount of which at ratios Na_2CO_3 : $Na_2SO_4 = 1.0$; 0.8: 0.2; 0.5: 0.5 increases from 1.97-4.68 to 3.66-5.78 and 8.05-12.67 kg, respectively. When the ratio $Na₂CO₃$: $Na₂SO₄$ 0.5: 0.5, the solid phase is also formed at a lower degree of evaporation - 40%. The maximum amount of solid phase 8.05-12.67 kg is formed when the ratio of the initial components is 0.5:0.5 and the degree of evaporation is 60-80%.

To determine the mineralogical composition of sediments formed during causticization, the Xray phase research method has been used [10, 11].

As the X-ray diffraction patterns of sediments show (Fig. 4 and Table 5), the main constituent mineral is $CaCO₃$, the amount of which is 35-80%. Its content increases with a growth in the amount of $Na₂SO₄$ in the initial soda-sulfate solution. The content of $CaSO_4 \cdot 2H_2O$ practically does not depend on the ratio Na_2CO_3 : Na_2SO_4 . With the ratio Na_2CO_3 : $Na_2SO_4 = 0.5: 0.5$, the burkeite content is more than 27%.

> With increase in the $NaOH$ content in the circulating solution, the filtration rate decreases at all selected ratios of $Na₂CO₃$: $Na₂SO₄$ and fluctuates in the range 103.8-318.4 kg / m2h, and the highest rate is appeared with the ratio Na_2CO_3 : $Na_2SO_4 = 0.8$: 0.2 . With these ratios in the studied intervals of variation of the $NaOH$ concentration in the circulating solution, the filtration rate ranges within 215-318 kg / m2 h, the moisture content of the sediment is 8-28%,L:S in the suspension is 7-8:1. The content of ions $OH^-, CO_3^{2-}, SO_4^{2-}$ is (wt.%); 3.30-6.70, 2.1-2.4 and 0.11 - 0.64, respectively (Table 1-3).

Fig. 3. Kinetics of suspension clarification. Na_2CO_3 : Na_2SO_4 ratio: 0.5:0.5

Table 2. Influence of technological parameters on the ionic composition of the causticization suspension filtrate

** Concentration of milk - 18%*

*** Process temperature-90^oC*

**** Process duration -90 min.*

Table 3. Ionic composition of the water-soluble part of the dry solid phase of the causticization suspension

* Concentration of lime milk - 18%

** Process temperature-90°C

*** Process duration -90 min.

Fig. 4. X-ray pictures of samples. Sample numbers correspond to those in Table 1.

The clarification rate of the suspensions after causticization was high and after 15-30 minutes it was 70%. As a result of clarification, a dense

sediment with L:S= 1: 2-4 was formed, which ensured better filtration and washing of the sediment.

Subsequently, after the filtration process with an increase in the degree of evaporation of the liquid phase to 80%, the content of OH^- - ions in it (Table 6) gradually increases to 28.29; 19.07 and 28.67%. The content of SO_4^{2-} and CO_3^{2-} ions first increases to reach a degree of evaporation of 40% and then at a degree of evaporation of 80% decreases to 1.01, 0.92 and 0.45 at ratios of Na_2CO_3 : $Na_2SO_4 = 1.0$; 0.8: 0.2; 0.5: 0.5 respectively.

The chemical composition (Table 7) of the sediments consisted mainly of sodium sulfates and carbonates and an insignificant amount of sodium hydroxide. Depending on the conditions of precipitation formation, the content of ions fluctuates in the intervals, (wt.%): $Na⁺ - 22.55 48.68; OH^- - 0.03 - 4.25; CO_3^{2-} - 1.08 49.5; SO_4^{2-} - 1.73 - 65.0[8-9].$

As shown by the elemental composition of the samples according to DS (table 8 and Fig. 5), the sludge consists of Ca, O and C and the sediments are from Na, O, S and C .

Microscopic analysis of sediments (Fig. 2) showed the presence of crystals $Na₂SO₄$, $Na_2CO_3 \cdot H_2O$ and $Na_2CO_3 \cdot 2Na_2SO_4$ with an average size of 252.3 μm, depending on the technological parameters of the process [10-12].

As the X-ray diffraction pictures of sediment samples (Table 9 and Fig. 6) 3 and 4 show, the sample consists mainly of $CaCO₃$ and $Na₂CO₃$. $H₂0$, respectively 61 and 72%, in samples 7 and 10 the content of burkeite is at least 57%.

Fig. 7 shows a derivatogram of causticizing sludge and sediment, which formed during evaporation.

Thermogravimetric analysis of curved (DTG) sludge samples shows that its intensive decomposition is observed mainly in two temperature ranges. The first temperature range of decomposition is 53-244^oC; the second is 255- 790°C (Fig. 7, Table 10).

N ₂	Ratio $Na2CO3$:Na ₂ SO ₄	Degreeofevaporation,%	The amount of solid phase,%, of the total initial mass	L: S at the end of the evaporation process	Filtration rate, kg / m^2 -h	Sedimentmoisture,%
	1:0	20	Transparentliquid			
2		40	Transparentliquid			
3		60	1.97	19:1	180	27.4
4		80	4.68	3.5:1	280	10.29
5	0,8:0,2	20	Transparentliquid			
6		40	Transparentliquid			
		60	3.66	10:1	227	23.74
8		80	5.78	3:1	415	8.30
9	0,5:0,5	20	Transparentliquid			
10		40	1.60	38:1	65	17.24
11		60	8.05	4:1	374	12.50
12		80	12.67	0.6:1	971	4.80

Table 4. Influence of the degree of evaporation on the aggregate state of the system and filterability of the formed sediment

Table 5. Mineral content (wt%) in samples

**sample numbers correspond to those in Table1*

Table 6. Ionic composition of liquid phase after evaporation

Table 7. Chemical composition of sediments formed after evaporation

Table 8. Elemental composition of samples according to the energy dispersive spectrum of samples

Table 9. Mineral content in samples, wt%

Mineralcodeandname			Samplenumbers.*		
				10	
01-078-4615 $Ca(CO3)$	61	10			
01-078-6180 Ca(SO ₄) \cdot H ₂ O	18	11			
01-070-0845 Na ₂ CO ₃ .H ₂ O	14	72			
01-074-1085 Na ₂ (SO ₄)(CO ₃) H ₂ O					
01-088-2051 Ca(S ₂ O ₄)(H ₂ O) ₄					
01-085-1732 $Na2(SO4)(CO3)$			57	82	
01-086-0803 Na2(SO ₄)			26	18	
01-072-0161 Na ₂ S ₂ O ₃					

** sample numbers correspond to those in Table 4*

Fig. 7. Derivatogramm of the sample

Intensive decomposition occurs in the second temperature range, where 18.8% of the substance is decomposed.

To calculate and select equipment, as well as to determine the sequence of stages of the proposed production, it is necessary to know the rheological properties of liquids and suspensions formed in the technological stages [13].

Within the studied range of variation of technological parameters, the viscosity and density change in the intervals 4.10-156.5cpz and $1.170 - 1.517$ g/sm³, respectively (Table 11). It

should be noted that at 30°C with an increase in the degree of evaporation of more than 60%, a sharp increase in viscosity is observed at all three ratios of $Na₂CO₃$: $Na₂SO₄$; however, with an increase in temperature over 60°C, the effect of the degree of evaporation (solution concentration) is leveled. The study of the effect of temperature on the viscosity of the suspension showed that at a ratio of Na2CO3: Na2SO4 -1.8: 0.2 at a temperature of 900C decreased 2.91 times, decreased from 13.28 to 4.56 centipoise, and at a temperature of 300C this indicator decreased by 14.68 times from 111.6 to 7.6 centipoise.

Sample numbers	Viscosity, cps				Density, g/sm ³		
correspond to the numbers in	30° C	60° C	90° C	30° C	60° C	90° C	
Table 4.							
1.	17.60	9.5	4.40	1.201	1.190	1.180	
2.	17.20	8.81	4.30	1.230	1.218	1.205	
3.	29.13	13.01	6.10	1.327	1.305	1.292	
4.	156.50	22.5	9.50	1.517	1.505	1.480	
5.	13.28	8.81	4.56	1.156	1.142	1.131	
6.	16.90	10.11	4.10	1.205	1.193	1.186	
7.	26.40	11.70	5.60	1.287	1.275	1.260	
8.	111.60	22.20	7.60	1.485	1.457	1.435	
9.	14.90	9.11	4.56	1.195	1.187	1.170	
10.	16.40	9.20	4.60	1.230	1.217	1.200	
11.	18.16	10.11	4.78	1.250	1.240	1.225	

Table 11. Rheological properties of evaporated solutions of caustic soda

4. CONCLUSION

Thus, the conducted studies have established that in the range of mass ratios Na_2CO_3 : $Na_2SO_4=$ (0,8-0,5):(0,2-0,5), with a general norm of Ca(OH)² not more than 100% relative to carbonate sodium, circulation of a circulating solution containing $3-7\%$ NaOH. At a temperature at least 95°C for at least 2 hours, a movable with a sufficiently acceptable filtration rate is formed to obtain a weak transparent lye of the composition (wt,%): $Na^+, OH^-, CO_3^{2-}, SO_4^{2-}$ 6.07 − 10.81; 2.78− 6.70; 2.1− 4.65; 2.1−

4.65 and 0.49-0.64, respectively. This allows, during evaporation, to obtain rapidly settling large crystals of $Na_2CO_3 \cdot 2Na_2SO_4$, Na_2CO_3 , Na_2SO_4 and a concentrated sodium hydroxide solution.

The results of studying the rheological properties of transparent filtrates show that it is desirable to pump them at a temperature not lower than 60° C.

ACKNOWLEDGEMENT

Authors acknowledge Doctor of technical sciences, senior scientific researcher Bokhodir E. Sultonov from Namangan State University due to his contributions in this article.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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