Math Modeling of Soda-Potash Solutions Processing at RUSAL Achinsk

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Abstract

Due to the depletion of reserves of specification-grade ores of the Kiya-Shaltyrsky nepheline mine and the Mazulsky limestone mine, RUSAL Achinsk JSC receives raw materials with a high variability of chemical compositions in terms of Na, K, S, Cl, and Al. The raw materials supplied are heat treated to obtain a semi-product, i.e., sinter. Further on, during the hydro-chemical processing of the sinter by the process solutions of the refinery, an imbalance in ions $2Na^+$, $2K^+$, SO_4^{2-}, CO_3^{2-}, Cl^- occurs. For this reason, there are certain complications in processing a soda-potash solution to obtain commercial products (i.e., calcined soda, potassium sulfate) in the Calcined Soda Shop (CSS) of the alumina refinery. To solve this problem the specialists of RUSAL Engineering and Technology Center developed an app for the on-line calculation of the material balance in the workshop which allows the rapid evaluation of the key technological indicators of the process. The app is able to carry out detailed material balance calculations for the main areas of the workshop (concentration of solution, crystallization of monohydrate soda, crystallization of potassium sulfate, crystallization of anhydrous soda), plot solubility diagrams of salts in the $Na^+|K^+–CO_3^{2-}–SO_4^{2-}–H_2O$ system and provide recommendations on technological process management. In 2021, the app was successfully fully implemented at the production site of JSC RUSAL Achinsk.

Keywords: Math modeling, Salt solubility diagram, Material balance, Soda-potash solutions

1. Introduction

JSC RUSAL Achinsk (AGK) is the Russia's largest enterprise processing nepheline ore to alumina and by-products (raw materials for cement, calcined soda, and potassium sulfate). The refinery uses millions of tonnes of soda and limestone annually. Nepheline ore is characterized by a wide variety of chemicals (Al_2O_3, Na_2O, K_2O, SiO_2, CaO, Fe_2O_3, SO_3, MgO, TiO_2, Cr_2O_3, etc.) and minerals (nepheline, analcime, orthoclase, natrolite, amesite, kaolinite, calcite, goethite, magnesite, pyrite, etc.) compositions [1]. Irregular distribution of these minerals in the ore of the Kiya Shaltyrsky nepheline mine, as well as complexity of raw material blending (millions of tonnes annually), result in an uneven supply of alkalis, carbonates, and sulfates into the production process. Additionally, due to exhaustion of the Mazulsky limestone mine, many detrimental minerals get into the process, e.g., pyrite (FeS_2), kaolin ($Al_2O_3·2SiO_2·2H_2O$), silica (SiO_2), etc. The impact of numerous factors on downstream processing stages (i.e., mix preparation, sintering, sinter leaching, desilication, precipitation, carbonation) results in a high variability of the ionic composition of the soda-potash solution (an intermediate product of alumina production), which is directed to extracting the soda products to the Calcined Soda Shop (CSS).

2. Method of Processing Soda-potash Solutions

A soda-potash solution is an intermediate product of the hydrochemical area of alumina production and contains mainly cations $2Na^+$, $2K^+$ and anions $A1O_2^-$, HCO_2^-, CO_3^{2-}, SO_4^{2-}, SO_3^{2-}, OH^- Cl^- in the water (dissolvent). As per the current process, the soda-potash solution enters the processing unit for neutralization where caustic alkali (special solution with a high con-tent of free caustic alkali, i.e., NaOH, KOH, prepared in the causticization area) is added to the solution to neutralize HCO_2^- ions by an exchange reaction. The composition of the solution from the neutralization unit corresponds to the $Na^+|K^+–CO_3^{2-}–SO_4^{2}–Cl^-–AlO_2^-–OH^-–H_2O$ seven-component system, which is not well studied [2,3]. It is known that only high concentrations of anions $A1O_2^-$ and OH^- in the solution influence the salt solubility [4], but usually when $A1O_2^-$ content in the soda-potash solutions is low: only some sections of the multicomponent system have been studied.

The soda-potash solution, which is directed to the CSS from neutralization, is then preconcentrated (excessive water is removed to achieve the target solution density and salt concentrations). It is further supplied to isothermal crystallization. At 95–100 °C, i.e., slurry temperature in evaporation trains, the solution is evaporated to achieve the required concentration, which is higher than soda saturation, to obtain a wet $Na_2CO_3·H_2O$ product (monohydrate soda, which is dried to anhydrous soda in drum driers). Figure 1 shows the main processes of the CSS.

As can be seen in Figure 1, a mother solution (solution after the removal of monohydrate so-da) is directed to extraction of potassium sulfate (K_2SO_4) by adiabatic isohydric crystallization, i.e., the solution is supersaturated by cooling below 40 °C. However, the precipitation of berkeyite ($2Na_2SO_4·Na_2CO_3$) or glaserite ($Na_2SO_4·3K_2SO_4$) should be avoided, as they are undesirable products and are not required in the salt market.

After sulfate crystallization, the mother solution goes to isothermal crystallization where the solution is evaporated up to a higher concentration than the soda saturation point in order to obtain a commercial product, i.e. Na_2CO_3 (anhydrous soda). After evaporation the mother solution is treated as a spent solution and is mixed with the mother solution from monohydrate evaporation to prepare the feed solution for sulfate crystallization. In other words, the process for salt extraction requires availability of the spent solution and implies balanced operation of the evaporation equipment to ensure complete processing of the soda-potash solutions.

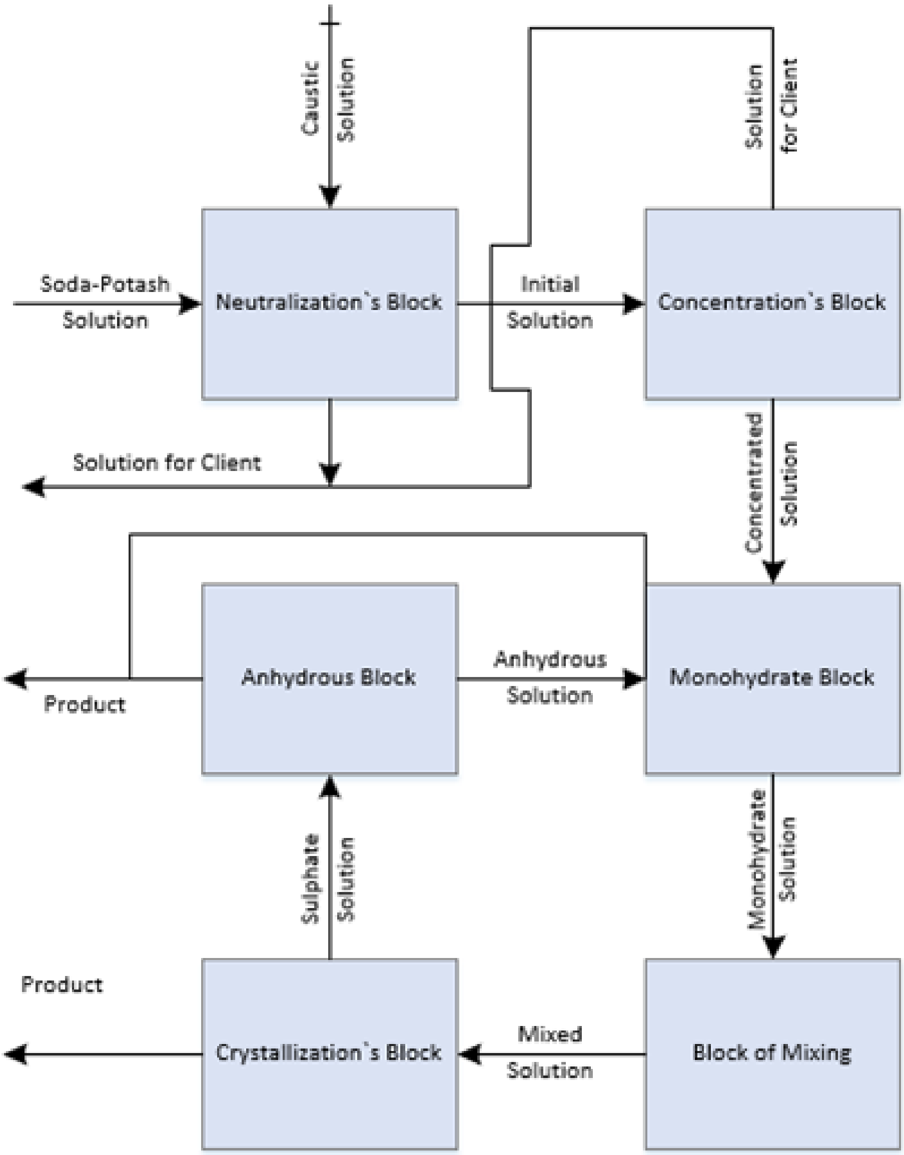

Figure 1. Process flow diagram in the calcined soda shop.

Under existing AGK's operating conditions to obtain commercial products, various methods of salt separation are applied (by rearranging the blocks shown in Figure 1) using the salt solubility diagrams in the $Na^+|K^+–CO_3^{2-}–SO_4^{2}–H_2O$ four-component system (as part of the $Na^+|K^+–CO_3^{2-}–SO_4^{2}–Cl^-–AlO_2^-–OH^-–H_2O$ seven-component system) within a wide range of temperatures (30–110 °C). This part of the system has been well studied by a number of researchers, namely, Varlamov M. L., Benkovsky S. V., Timoshenko V. V., etc. The system serves as a basis for the processes of salt extraction from soda-potash solutions [4, 5].

Figure 2 shows the general view of a part of the four-component system on cations $2K^+$ (= 100–$2Na^+$) and anions SO_4^{2-} coordinates (plotting the nodes and eutonic lines) at an average annual temperature of the soda-potash solution fed to the CSS (82 °C).

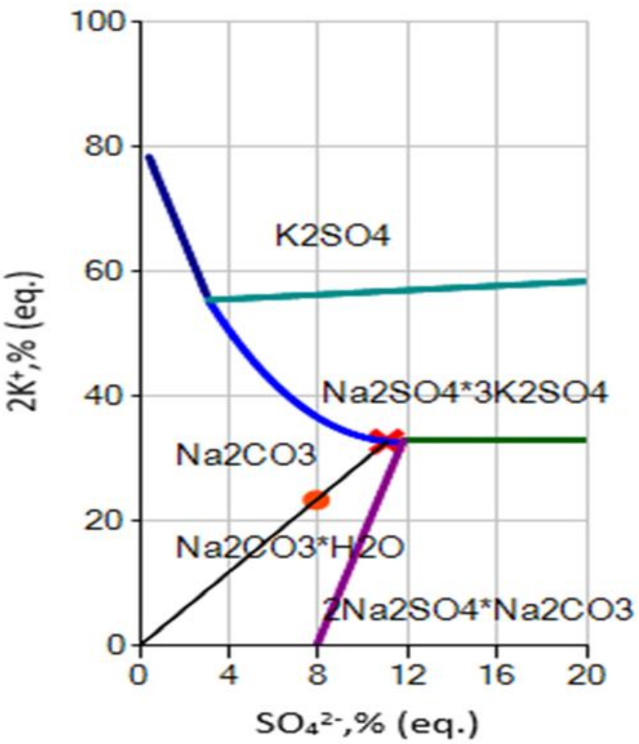

Figure 2. Part of the salt solubility diagram in the $Na^+|K^+–CO_3^{2-}–SO_4^{2}–H_2O$ system at 82 °C.

Figure 2 displays the point of the feed solution and crystallization ray of monohydrate soda (drawn from the origin [0, 0]) expressed graphically on the salt solubility diagram. Further tracing of the salt crystallization rays is performed in a similar fashion.

If the ionic composition of the soda-potash solution is unstable, anions CO_3^{2-}, SO_4^{2-}, SO_3^{2-}, and Cl^- are accumulated in the recycling mother solutions, thus resulting in disruptions of salt separation, imbalance of the circulating flows, low efficiency of the evaporation equipment, and deterioration of the product quality. Therefore, the processing of soda-potash solutions is characterized by a number of the following specific features:

1. Quality (i.e., containing a minimum amount of impurity salts) in the final commercial products (calcined soda, potassium sulfate) can be obtained only by salt crystallization within narrow regions of the salt solubility diagram. If the composition of the mother solution falls into the double salt crystallization region, the product quality significantly deteriorates.
2. Enhancement of the production process or salt crystallization at the eutonic line borders increases the fine fraction in the commercial product, thus affecting the degree of the solution decomposition (filters get clogged, lower slurry density results in increasing moisture and im-purities in the salt, etc.). For this reason, salt crystallization should be stopped before it reach-es the eutonic lines.
3. Due to high variability of the chemical composition of the soda-potash solution the production process becomes dynamic and requires prompt computation of a number of process and chemical parameters to calculate the ion balance of the solutions.
4. Under unfavorable process conditions, the amount of crystallized salts can reduce significantly, i.e. solution processing deteriorates; therefore, if anions CO_3^{2-} and SO_4^{2-} are unbalanced, valuable salts (K_2CO_3, K_2SO_4) will go to a different area of the refinery instead of the product.

Accordingly, the operating personnel shall solve an important task, i.e., promptly calculate the material balance of the area in case of significant changes in the composition or flow rate of the soda-potash solution supplied to the CSS. Prompt (real time) forecast of the material balance in the workshop allows for preparation of the equipment for the processing of the solution, the evaluation of the product quality, the identification of bottlenecks in the process, and consequently the reduction of the cash cost of the products [6, 7].

3. Data Analysis of the Chemical Composition of the Process Solutions

The main reason for the changes in the product quality is unstable chemical compositions of the solutions. The variability of the chemical compositions of the solutions can be assessed using mean-square (standard) deviation (MSD) and variation coefficient (VC). Table 1 presents mean-square (standard) deviations and variation coefficients for the salt contents monitored at the refinery (gpL). These values were calculated based on the statistical processing of the input solution data from the refinery for 2021.

Table 1. Standard deviation and variation coefficient for solution components.

Solution component	Process solutions							
	Soda solution		Monohydrate mother solution		Sulfate mother solution		Anhydrous mother solution	
	MSD	VC	MSD	VC	MSD	VC	MSD	VC
Na_2CO_3	14.9	12.1	2.11	9.6	1.03	5.9	1.2	8.5
K_2CO_3	3.4	18.2	1.03	13.3	3.58	21	1.23	23.3
K_2SO_4	3.57	16.9	0.63	9.7	1.89	44	0.66	11.6
KCl	0.46	26	0.1	13.9	0.47	27.7	0.19	8.9

Table 1 proves that at VC > 10 % for K_2CO_3, K_2SO_4, and KCl are unstable salts in the solutions. So, changes in the amounts of cations 2K+ and anions CO_3^{2-}, SO_4^{2-}, SO_3^{2-}, Cl^- in the process solutions influence salt extraction. To control the ion balance, prompt computation of Janecke indices can be applied. Janecke indices are equivalent percents, i.e., ratio of equivalents of the salt, which makes up a system, to the sum of the salt equivalents, in which the sum of cations, as well as the sum of anions, are equal to 100. The CSS operation experience proved that real-time material balance can be calculated using a graphical method of calculating the material balance in the CSS based on salt solubility diagram in the $Na^+|K^+–CO_3^{2-}–SO_4^2–H_2O$ system for the actual range of process solution temperatures, i.e., 35–110 °C. Graphical plotting and calculation of the solution parameters with the solubility diagrams is an effective method for improving the current production processes. This method has the following ad-vantages: computational efficiency/simplicity, process visualization, and reliability of the obtained results.

4. Prompt (Real Time) Calculation of the Material Balance

In order to provide the rapid calculation of the physical and chemical processes of salt separation, in 2021 the specialists of RUSAL Engineering and Technology Center developed an app for the consolidation of the material balance in the CSS. This app adjusts the $Na^+|K^+–CO_3^{2-}–SO_4^2–H_2O$ four-component system for the salt extraction under the conditions of the Achinsk alumina refinery [8]. Due to the low content of ions Cl- in the feed solution, the current technology of the soda-potash solution processing does not involve extraction of potassium chloride, which results in a number of process considerations\issues, i.e. a limited number of evaporation/crystallization vessels, extraction of impurities ($A1O_2^-$, HCO_2^-, Cl^-, etc.) with the product (while maintaining the quality, which is affected, above all else, by the hygroscopic moisture of the salt precipitate), setting objectives for the ratio of ions $2Na^+$ and $2K^+$ (calculation of Janecke indices) in the process solutions, etc. All these factors were considered during the development of the application for real-time calculation of the material balance in the CSS.

To apply a graphical calculation method, the solubility diagram of salts in the $Na^+|K^+–CO_3^{2-}–SO_4^{2}–H_2O$ system was divided into the crystallization field of each salt at various temperatures (see Figure 2): each curve was described by a mathematical equation, i.e. a line or second or-der polynomial; double or triple eutonic points were distinguished (nodes of overlapping of salt crystallization fields), a graphical user interface was developed to display the calculated values on the app screen. Figure 3 shows an app screen shot.

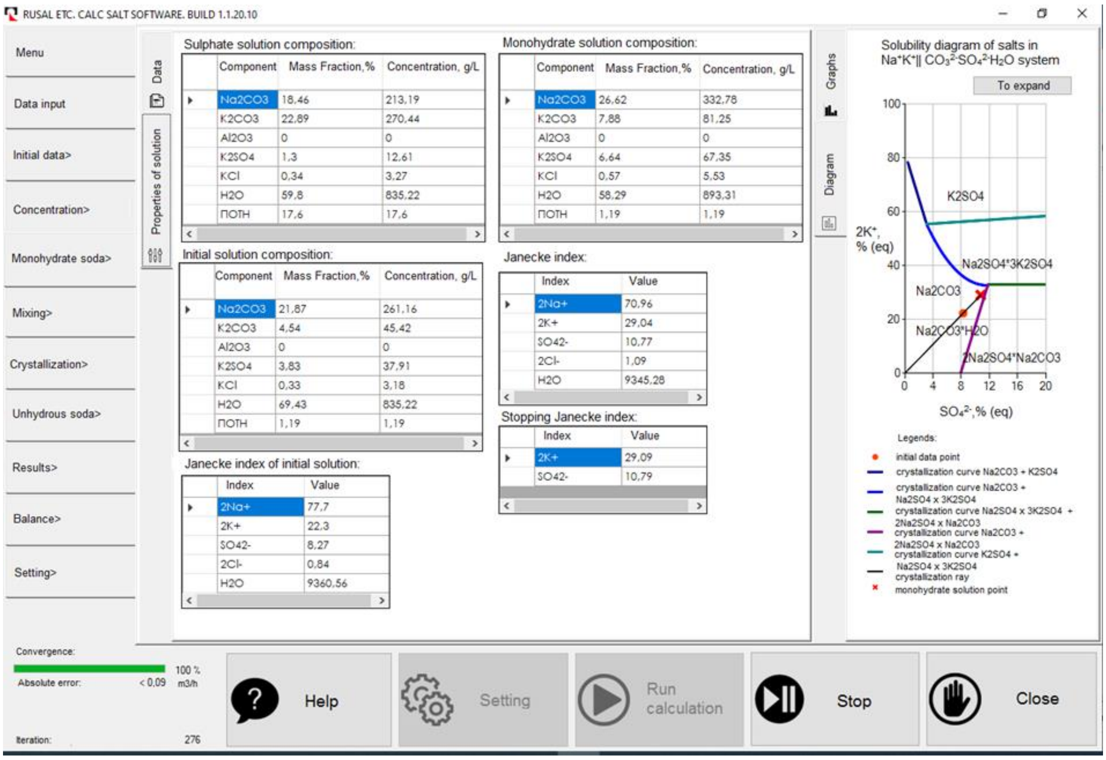

Figure 3. App screen for calculating the material balance in the CSS.

For each process (neutralization, solution concentration, extraction of monohydrate soda, crystallization of potassium sulfate, and extraction of anhydrous soda), a salt solubility dia-gram is developed with due account of the temperature profile, density and composition of the solution and indicating points of solution compositions before and after salt extraction. Crystallization ray diagrams allows determining the region of salt precipitation, estimating the amount and quality of the salts, as well the composition of the resulting mother solutions, calculating Janecke indices for $2K^+$, $2Na^+$, SO_4^{2-}, CO_3^{2-}, $2Cl^-$ to assess the ionic balances of the solutions. Additionally, the app enables the following: calculation of the eutonic lines based on the actual temperatures of salt separation, mass and volume flows, densities of the solutions based on their chemical compositions, compositions of the crystallized solid phases; dis-play the estimated values on the plots/graphs and diagrams; automatically request data from the AGK control system (DeltaV™, Emerson) powered by OPC client-server architecture; aa well as performing other tasks.

Figure 4 displays a structural diagram of the app operation. As Figure 4 shows, “Selecting a data source” block represents various methods of data input, i.e., request of the current data from

DeltaV™ database, request of the data from DeltaV™ database and preliminary data cleaning\filtering (sliding window, local sliding window, exponentially weighted window), manual input (to use the app for modelling the process options). The data are collected, filtered and processed using API-server, which functions in RUSAL's integrated information network. The "Setting up app before calculation" block represents a pre-initialization of all variables to verify the conformity of the initial data to the calculation parameters. The "Material balance calculation mode of app" block represents the iterative calculation of the material balance of the process area by the semi-implicit method. The "Output of calculation results" block informs the user of the current process of consolidating the material balance, namely, by displaying graphs\diagrams, intermediate values, solubility diagrams for each area, etc. Developed computational algorithms, graphical interface, and data interchange tools provide for easy and user-friendly data input, online calculation of the main process parameters, forecast of the ionic compositions of the spent solutions. All parts of client-server application ex-change data via JSON data-interchange format, which enables to transmit reference information to the interface or to RUSAL's related systems.

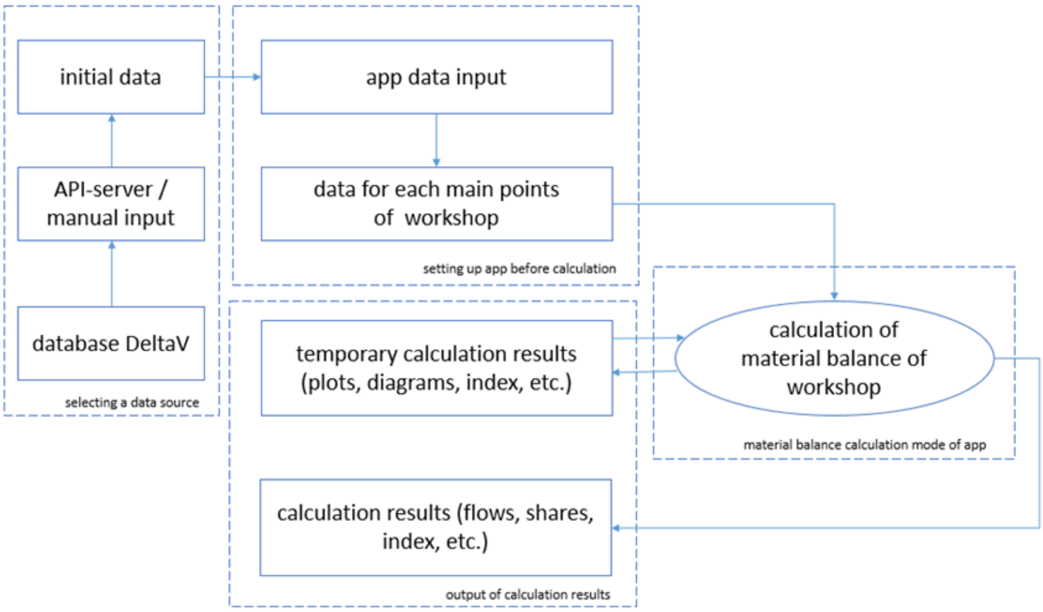

Figure 4. Data flows in the app to calculate the material balance in the CSS.

5. Use of app for Calculating the Material Balance

Starting from 2014-, due to depletion of ores of the Kiya-Shaltyrsky nepheline mine and the Mazulsky limestone mine, anions SO_4^{2-} and SO_3^{2-} are increasing and cations $2K^+$ are decreas-ing in the process solutions at the refinery. If SO_4^{2-} -ion content in the CSS flows increases, potassium carbonate sesquihydrate is added to the process. It enables the plant to achieve a balance between $SO4^{2-}$ and $2K^+$ ions and transfer SO_4^{2-} ions to the product, i.e. potassium sul-fate K2SO4 (lab tests on extracting potassium sulfate showed that improved efficiency of K_2SO_4 extraction from the process solutions requires a specific concentration ratio of K_2CO_3 to K_2SO_4 in the sulfate solution, i.e. 1.2–1.4 U). For this reason, assessing the amount of $K_2CO_3 \cdot 1.5H_2O$ that should be added to the process to maintain the balance of SO_4^{2-} and $2K^+$ ions, as well as calculating theoretically possible production of high-quality calcined soda are tasks, which are typical for this refinery process. Figure 5 shows the results of the calculations of theoretically possible production of high-quality calcined soda and dosage of potassium car-bonate sesquihydrate (t/h) to the process performed with the created app. The results are cal-culated provided that ratio of K_2CO_3 to K_2SO_4 in the sulfate solution is equal to 1.25 (set point) with K_2SO_4 amount of 16.8-22.8 g/L and K_2CO_3

amount of 14.2-18.2 g/L in the initial soda-potash solution. The calculation results (see Figure 5 (a)) show that the amount of mon-ohydrate soda (high-quality soda) is 69–71 % when the K_2CO_3 content in the initial solution increases. At the same time, the required addition of potash to the process decreases from 3 to 0 t/h. If the K_2SO_4 content increases in the initial soda-potash solution, the production of high-quality soda reduces from 71 % to 51 %, thus the amount of potash added to the process should be increased up to 5 t/h (see Figure 5 (b).

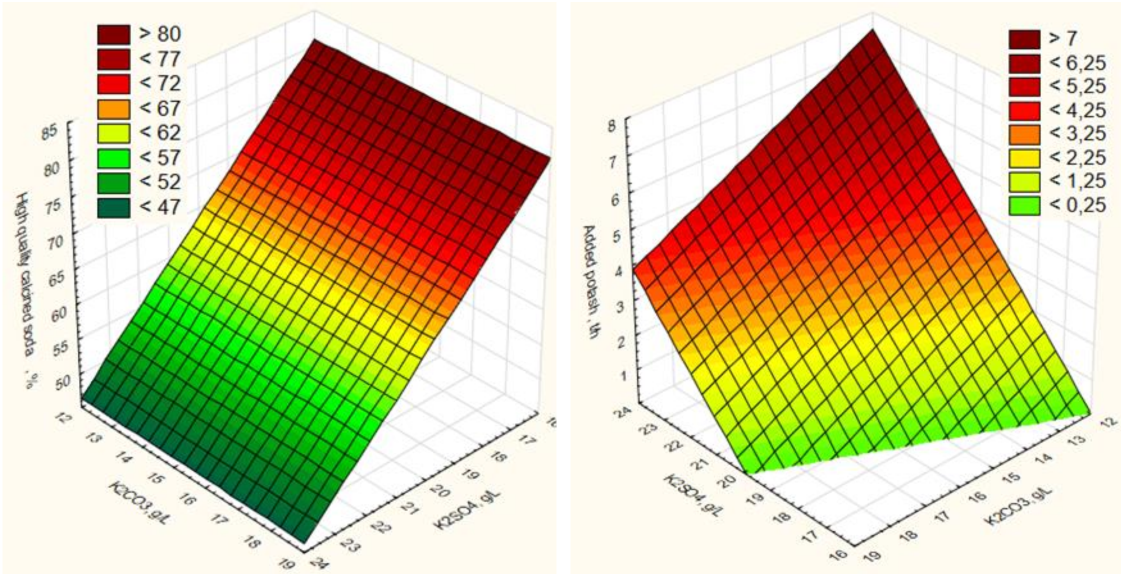

Figure 5. Calculations in the app: theoretically possible production of high-quality soda (a) and potash dosage (b) depending on K_2CO_3 and K_2SO_4 content (g/L) in the feed soda-potash solution.

6. Conclusion

The chemical composition of the ore, as well as its variability due to the variable compositions of the raw materials, have a marked impact on production of AGK's by-products, i.e., calcined soda and potassium sulfate. The results obtained by statistical processing of the data of CSS's solutions explain high mean-square (standard) deviations and variation coefficients of the salt compositions in the liquors. The work has concluded that the instability issue can be over-come by using real-time calculations of the material balance in the process area and prompt preventive measures in changing $2Na^+$, $2K^+$, SO_3^{2-}, SO_4^{2-}, CO_3^{2-}, Cl^- ions balance in the process liquors. Such measures include temporary removal of excessive liquor from the process, addition of potassium carbonate sesquihydrate, use of additional evaporation vessels, etc. The app for calculating the material balance was used at the Achinsk refinery in 2021-2022. The performance achieved enabled the following conclusions to be drawn.

Calculation of the material balance in the CSS area is an efficient, quick, easy, and reliable solution for promptly establishing the ionic balance in the solutions under conditions of changing salt composition in the feed soda-potash solution. Moreover, the app provides recommendations to the operator and process engineer on possible preventive solutions.

Use of the graphical method of calculating the material balance based on the salt solubility diagram in the $Na^+|K^+–CO_3^{2-}–SO_4^{2}–H_2O$ system is a simple and easy-to-view method for enhancement of the current methods for processing aqueous solutions.

App features and functionality enable the operator to assess the detailed information on the performance of each area at the refinery based on the input data on flow rates and chemical compositions, and thus predict the operation of the equipment.

7. References

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