The Austrian Journal of Technical and Natural Sciences, No 5–6
ISSN 2310-5607

PREMIER Publishing
ppublishing.org

DOI:10.29013/AJT-25-5.6-120-126

STUDY OF THE REMOVAL OF SODIUM AND CALCIUM IONS FROM SATURATED DIETHYLENE GLYCOL (SDEG) USING SODA ASH SOLUTIONS

Mamarasulov B. S. [1]***, Koshanova B. T.*** [1]***, Erkaev A. U.*** [1]***,***
Reymov A. M. [2]***, Reymov K. D.*** [2]

[1] Tashkent Institute of Chemical Technologyт

[2] Karakalpak State University named after Berdakh

Cite: *Mamarasulov B. S., Koshanova B. T., Erkaev A. U., Reymov A. M., Reymov K. D. (2025). Study of the Removal of Sodium and Calcium Ions from Saturated Diethylene Glycol (SDEG) Using Soda Ash Solutions. Austrian Journal of Technical and Natural Sciences 2024, No 5–6.* https://doi.org/10.29013/AJT-25-5.6-120-126

Abstract

This paper explores the process of removing sodium and calcium ions from saturated diethylene glycol (SDEG), used in natural gas dehydration. It was established that during operation, SDEG accumulates impurities, including sodium and calcium chlorides, which affect its efficiency. Studies were conducted on the solubility of these salts in DEG solutions at varying temperatures and concentrations. It was shown that calcium mainly remains in solution during evaporation, complicating regeneration. A two-stage purification process is proposed: preliminary precipitation of calcium as carbonate using a 30% soda ash solution, followed by evaporation and removal of sodium chloride. X-ray diffraction analysis and chemical composition of the precipitates confirm the effectiveness of the proposed method. The developed approach enhances DEG regeneration quality and prevents impurity buildup in the system.

Keywords: *diethylene glycol, saturated diethylene glycol (SDEG), regeneration, soda ash, sodium chloride, calcium chloride, solubility, precipitation, natural gas purification, calcium carbonate*

Introduction

The purification and dehydration of natural gas are crucial stages in the preparation of raw materials for transportation and processing. One of the most effective absorbents used for moisture removal is diethylene glycol (DEG), which possesses high hygroscopicity as well as thermal and chemical stability (Korneev A. A., Yakovlev I. M., 2004; Grishin A. M., 2011). However, during operation, DEG becomes saturated with moisture and contaminated with inorganic salts, primarily sodium and calcium chlorides originating from formation water (Reznikov A. A., Pleshkov Yu. P., 1987). This leads to a decline in its absorption properties and necessitates regeneration (Perry R. H., Green D., 2007).

DEG regeneration processes involve the removal of moisture, volatile organic compounds, and mineral impurities. In recent years, particular attention has been paid to the removal of calcium and sodium ions, as their presence promotes salt deposition on equipment surfaces, reduces heat transfer efficiency, and increases the risk of corrosion (Akhmetov G. Kh., 2009; Marchenko A. V., 2017).

The literature describes various approaches to reducing salt concentrations in saturated DEG (SDEG), including evaporation, extraction, and chemical precipitation techniques (Chernyshev I. G., Titov V. P., 2006). It is known that calcium can be effectively removed from solution in the form of sparingly soluble calcium carbonate through interaction with carbonate-containing solutions such as soda ash (Na_2CO_3) (Chandrasekaran V., 2019). This method is widely used in water treatment and in the purification of industrial process solutions (Chandrasekaran V., 2019).

The solubility of sodium and calcium chlorides in water-glycol systems has been thoroughly studied in several works (Knaebel K. S., 2006; Kovács G., Vatai G., 2010; Aliev I. A., Mukhamedov Sh. D., 2005). It has been established that $CaCl_2$ exhibits significantly higher solubility in DEG compared to NaCl, thereby necessitating a staged approach to their removal. The use of refractometric methods to monitor DEG concentration and salt content is also described in the literature as an effective analytical tool (Aliev I. A., Mukhamedov Sh. D., 2005; Mamarasulov B. S., Yuldashev N. Kh., Begdullaev A. K., Reymov K. D., Toirov Z. K., Erkaev A. U., 2022).

Thus, modern research confirms the relevance of an integrated approach to DEG regeneration, with a focus on preliminary precipitation of calcium ions followed by the removal of sodium chloride. This enables a significant improvement in absorbent efficiency and extends the operational life of processing equipment.

Nevertheless, during operation, DEG inevitably becomes saturated with moisture and various impurities, including salts, organic compounds, and suspended solids, which decrease its effectiveness. To restore the operational performance of diethylene glycol, a regeneration process is employed that removes unwanted components and returns DEG to the production cycle.

Objects and Methods

Formation water contains various salts (NaCl, $CaCl_2$, $MgCl_2$, etc.) that can interact with saturated diethylene glycol (SDEG).

At gas treatment facilities – specifically, at the integrated gas treatment unit (IGTU), where natural gas is separated from formation water and gas condensate – salt deposits also precipitate on the internal surfaces of equipment. The chemical and mineralogical composition of these deposits was determined, and micrographs were obtained. The corresponding data are presented in Table 1.

Table 1. *Ionic Composition of Deposits Precipitated on the Internal Surfaces of Equipment CGTP*

Name of sediment	Ionic composition of sediments, mass.%						
	Na	K	Ca	Mg	Cl	SO_4	H.o
Salt deposits CGTP	28.531	0.132	1.535	0.943	48.596	0.658	2.632

The solubility of sodium and calcium chlorides in diethylene glycol plays a significant role in natural gas purification processes. The low solubility of NaCl and the high solubility of $CaCl_2$ can lead to various issues related to contamination and salt deposition within equipment. Optimization of operating conditions and control over salt concentrations in the system can help minimize these problems.

To determine the relationship between DEG concentration and NaCl content, the solubility and density of the DEG–NaCl–H_2O system were studied over a temperature range of 20–100 °C.

Table 2 presents the solubility of sodium and calcium chlorides (DEG–NaCl–H_2O and DEG–$CaCl_2$–H_2O systems) at different temperatures.

Table 2. *Solubility of Sodium and Calcium Chlorides in DEG Solutions as a Function of Temperature and DEG Concentration*

Concentration DEG, %	Temperature, ^{0}C 20	40	60	80	100
	Solubility of Sodium Chloride, mg/l				
40	1643	1693	1714	1786	1850
50	1167	1433	1500	1571	1601
60	737	816	1000	1200	1267
70	632	737	895	947	1033
77	375	575	775	825	875
80	344	406	600	620	670
90	225	300	400	467	517
100	183	233	317	341	367
	Solubility of Calcium Chloride, mg/l				
40	1723	2525	2545	2725	2986
50	1503	1723	2004	2204	2604
60	822	982	1102	1182	1303
70	301	741	962	1082	1202
77	180	602	922	1002	1383
80	90	581	621	640	681
90	24	281	296	607	621

Results and Discussion

As the data show, with an increase in temperature from 20 °C to 100 °C, the solubility of sodium and calcium chlorides increases from 1,643 and 1,723 mg/L to 1,850 and 2,986 mg/L, respectively. At a 40% DEG concentration, within the range of 40–80% and up to 90%, the solubility of sodium and calcium chlorides decreases by a factor of approximately 4.17–5.64 and 4.31–8.99, respectively. The solubility of calcium chloride is 1.6 to 1.01 times higher than that of sodium chloride. However, in the original SDEG solution, the calcium chloride content is 3.7 times lower. Therefore, during the evaporation of SDEG to a DEG concentration of 90%, only sodium chloride precipitates, while calcium chloride accumulates in the regenerated DEG (RDEG), leading to an increase in its viscosity.

Table 3 shows that the refractive index of the system is affected by the DEG concentration and the presence of dissolved chloride salts.

Table 3. *Determination of Diethylene Glycol (DEG) Concentration Based on Refractive Index in Pure and Contaminated Solutions*

No.	Concentration DEG	Pure DEG n^{20}	Saturated Solution with Chloride Salts NaCl	$\Delta n^{20}_{\text{д}}/2$	CaCl$_2$	$\Delta n^{20}_{\text{д}}/2$	$\Delta n^{20}_{\text{д}}/2$	Determination of DEG Concentration in the Sample
1.	40	1.382	1.408	0.026	1.425	0.043	0.0345	
2.	50	1.394	1.416	0.022	1.429	0.35	0.0230	
3.	60	1.407	1.422	0.015	1.438	0.031	0.0210	

No.	Concentration DEG	Pure DEG n^{20}	Saturated Solution with Chloride Salts				$\Delta n^{20}_{Д}/2$	Determination of DEG Concentration in the Sample
			NaCl	$\Delta n^{20}_{Д}/2$	$CaCl_2$	$\Delta n^{20}_{Д}/2$		
4.	70	1.417	1.430	0.013	1.445	0.028	0.0170	
5.	77	1.425	1.435	0.010	1.449	0.024	0.0170	
6.	80	1.428	1.439	0.011	1.451	0.023	0.0170	
7.	90	1.437	1.445	0.008	1.457	0.020	0.0140	
8.	100	1.443	1.451	0.008			0.0100	
9.	SDEG	1.414						39.5
10.	30% evaporation	1.443						80.4
11.	40% evaporation	1.454						90.0
12.	50% evaporation	1.460						92.0
13.	RDEG	1.424						60.0

For example, when using a 40% DEG solution, the refractive index in the pure solution and in solutions containing sodium and calcium chlorides is 1.382, 1.408, and 1.425, respectively. The difference in refractive index ($\Delta n_{20}D$) between pure DEG and the sodium and calcium chloride solutions is 0.025 and 0.043, respectively, with an average difference of 0.0345. As the DEG concentration increases, both the $\Delta n_{20}D$ values and their average decrease to 0.008, 0.020, and 0.014, respectively.

Using this table, the DEG content in a solution can be quickly determined with any standard refractometer, with a margin of error of ±1.5%.

The studies have shown that dissolved calcium salts significantly affect the stages of spent SDEG purification. Therefore, prior to evaporation, it is necessary to investigate the decalcification process. Table 4 presents data on the effect of soda ash solution dosage on the evaporation process.

Table 4. *Effect of Soda Ash Solution Dosage on the Evaporation Process*

No.	Ratios SDEG: Soda Ash Solution (30%)	I stage		II stage (degree of allocation)	
		Degree of Precipitate Formation, %	Humidity, %	Sediment after (60%) evaporation, %	Humidity, %
1.	1:0.038	4.44	61.9	6.32	11.3
2.	1:0.061	6.20	58.0	9.35	10.5
3.	1:0.076	7.21	50.6	7.48	13.0
4.	1:0.083	7.31	72.4	8.34	4.06

The decalcification process was carried out according to the stoichiometry of the calcium carbonate formation reaction:

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl$$

A 30% aqueous solution of soda ash (Na_2CO_3) was used as the precipitating agent for calcium ions, with the SDEG-to-soda ash solution ratio ranging from 1:0.038 to 1:0.083.

According to the data presented in the table, during the first stage of precipitation, as the ratio of SDEG to soda ash solution increases from 1:0.038 to 1:0.076, the mass of the resulting precipitate (relative to the total mass of the initial components) increases from 4.44% to 7.21%, with a moisture content of 50.6–61.9%.

At a 60% degree of evaporation, up to 9.35% of solid phase is separated, with a moisture content not exceeding 13.0%.

Table 5 and Figure 1 present the elemental composition and X-ray diffraction (XRD) patterns of the unwashed precipitate formed:

in the first stage, during calcium ion precipitation with the addition of soda ash solution;

in the second stage, during the precipitation of sodium chloride from the decalcified SDEG solution in the evaporation process.

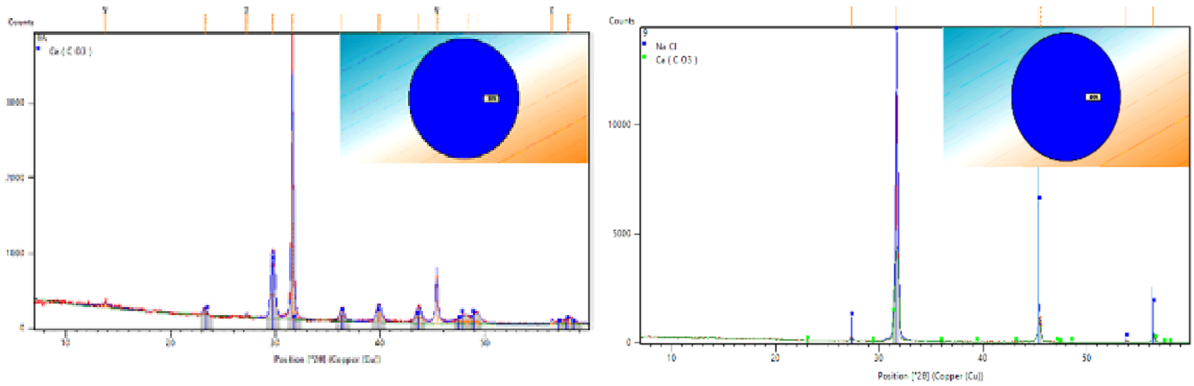
Table 5. *Elemental Composition of Samples (Sample Numbers Correspond to Table 4)*

Element	Spectors. massa %			
	I stage		II stage	
	1	2	3	4
O	45.6	39.3	8.9	0
Ca	33.8	41.6	2.0	0
Na	8.2	8.0	34.4	41.5
Cl	8.9	7.7	54.7	58.5
Mg	3.6	3.3		

As shown in Table 5, the precipitates formed during the first stage primarily contain calcium and oxygen. The contents of sodium, magnesium, and chlorine do not exceed 8.2%, 3.6%, and 8.9%, respectively.

In the second stage of precipitation, sodium and chlorine atoms dominate, with concentrations ranging from 34.4–41.5% and 54.7–58.5%, respectively. Meanwhile, the calcium content does not exceed 2.0%.

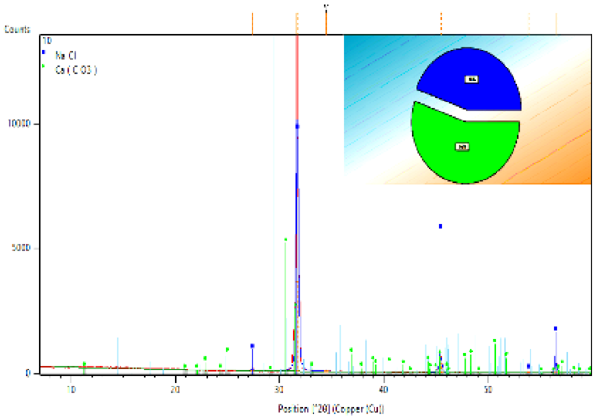
Picture1. *X-ray of samples*



Sample № 1 (I stage)

Sample № 1 (II stage)

Sample № 1 (II stage)



(Sample numbers correspond to those in Table 3)

Table 6. *Mineralogical Composition of the Samples*

No.	Name of mineral	Formula of mineral	Ref. code	Номер образцов		
				1 (II stage)	1’ (I stage)	1’ (II stage)
1.	Calcium carbonate	$CaCO_3$	01–080–9776		100%	
2.	Sodium chloride	NaCl	01–080–3969	100%		
3.	Calcium carbonate	$CaCO_3$	01–087–1863			55%
4.	Sodium chloride	NaCl	01–078–0751			45%

As can be seen from the X-ray diffraction pattern (Pic. 1), the precipitate formed during the first stage predominantly consists of calcium carbonate ($CaCO_3$), confirming the effectiveness of calcium removal through the addition of soda ash solution. In the second stage, following the evaporation of the decalcified solution, the main crystalline phase of the precipitate is sodium chloride (NaCl).

According to the obtained data, the separation process can be conventionally divided into two stages: first, calcium is removed as poorly soluble calcium carbonate; then sodium chloride is removed by evaporation. This allows for the production of a purified DEG solution, saturated with sodium and calcium chlorides, and enables regulation of its ionic composition according to specific technological requirements.

Conclusion

Sample analyses revealed that during the evaporation of spent saturated diethylene glycol (SDEG), sodium chloride crystals precipitate, while calcium chloride remains in solution. As a result of regenerated solution circulation, the Ca/Na ratio increases from 0.29 to 4.11, complicating further evaporation and deteriorating the absorption properties of the regenerated diethylene glycol (RDEG).

The conducted experiments confirmed the advantages of a staged separation process for calcium and sodium chlorides using inorganic precipitating agents – specifically, soda ash solutions. The kinetic patterns of SDEG evaporation after preliminary calcium ion precipitation were established under various residual pressure conditions.

References

Korneev A. A., Yakovlev I. M. (2004). Technology of preparation and processing of natural gas. – Moscow: Nedra, – 384 p.

Grishin A. M. (2011). Drying of natural gas: a tutorial. – Ufa: Ufa State Petroleum Technical University, – 118 p.

Reznikov A. A., Pleshkov Yu. P. (1987). Adsorbents and absorbents in the gas industry. – Moscow: Chemistry.

Perry R. H., Green D. (2007). Perry’s Chemical Engineers’ Handbook. 8th ed. Mc Graw-Hill.

Akhmetov G. Kh. (2009). Technology and equipment of gas processing plants. – Ufa: Ufa State Petroleum Technical University.

Marchenko A. V. (2017). Corrosion problems in the processing and transportation of natural gas. // Gas industry. – No. 7. – P. 22–25.

Chernyshev I. G., Titov V. P. (2006). Removal of salts from glycol solutions. // Petrochemistry. – Vol. 46. – No. 5. – P. 387–392.

Chandrasekaran V. (2019). Industrial Wastewater Treatment. CRC Press, – 405 p.

Kirk-Othmer (2004). Encyclopedia of Chemical Technology. – Volume 12: Glycols. Wiley-Interscience.

1Knaebel K. S. (2006). Glycol Dehydration of Natural Gas: A Do-It-Yourself Workshop. // Gas Processors Suppliers Association.

Kovács G., Vatai G. (2010). Effect of temperature and pressure on solubility of salts in glycols. // Desalination. – Vol. 251. – P. 145–150.

Aliev I. A., Mukhamedov Sh. D. (2005). Methods of analysis of water-glycol solutions. – Moscow: Chemistry.

Abdullayeva Sh.M., Mamarasulov B. S., Toirov Z. K., Erkaev A. U. (2023). Technology for the production of calcium chloride adsorbent used in gas drying from the distiller liquid of the kunhirot soda plant. IBET – volume 3, – issue 6, june. – P. 151–157.

Mamarasulov B. S., Yuldashev N.Kh., Begdullaev A. K., Reymov K. D., Toirov Z. K., Erkaev A. U. (2022). Study of the process of obtaining tableted calcium chloride from waste from the production of soda ash of Kungrad Soda Plant LLC. Universum; – No. 9 (102). September.

submitted 17.04.2025;
accepted for publication 01.05.2025;
published 29.05.2025

Contact: bekzod.mamarasulov.1993@gmail.com