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NON-CAKING AMMONIUM NITRATE MODIFIED WITH GLAUBER'S SALT: PROPERTIES AND RHEOLOGICAL BEHAVIOR OF MELTS

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Abstract

This study explores the effect of incorporating Glauber's salt, sourced from the Tumryuk deposit and processed at the KKRASI CHEMICAL plant, into ammonium nitrate (AN) melt in ratios ranging from AN: GS = 100:(0.25–3.0). The final compositions were characterized by nitrogen content varying from 34.28% to 33.25%, sodium oxide (Na_2O) from 0.02% to 1.11%, and total sulfur trioxide (SO_3) from 0.074% to 1.73%. The resultant granules were examined in terms of their elemental composition, strength, dissolution rate in water, and rheological parameters of their melts.

Keywords: *ammonium nitrate, Glauber's salt, anti-caking, granule strength, melt viscosity, solubility, composition*

Introduction

Feeding the rapidly growing global population remains a fundamental challenge for many countries. As of the 19^{th} century, the global population was about 1 billion (1830), rising to 4.9 billion by 1986, surpassing 6.1 billion in 2000, and reaching approximately 8 billion by 2015. Projections suggest the number will exceed 9 billion by 2050 (Dyson, T., 1995). Parallel to this population growth, the amount of arable land available per person has sharply decreased – from 0.24 hectares in the mid-20^{th} century to just 0.1 hectares by the century's end. By 2050, it may drop further to 0.08 hectares. This decline in agricultural resources is driven not only by demographic pressures but also by ecological degradation such as soil erosion, acidification, deforestation, desertification, and freshwater contamination (Kurbanov, E., Kuziev, R., 2001).

Similar conditions are seen in Uzbekistan, where approximately 25.7 million hectares of land are used for agriculture, of which only 3.73 million hectares are irrigated (Newspaper Narodnoe Slovo. 2016). These irrigated areas produce over 97% of the country's agricultural output. Uzbekistan ranks sixth globally in cotton production and achieved yields of 2.61 tons per hectare in 2015, producing 3.35 million tons in total. The country also maintains high levels of grain self-sufficiency, with 7.5 million tons harvested and an average yield of 5.5 t/ha (Practical Recommendations on Agriculture. 1996). Meanwhile, the population continues to rise-14 million in 1975, over 31 million in 2015-while irrigated land per capita has shrunk from 0.22 hectares in 1970 to 0.12 hectares today (Beglov, B.M. 2006; Vaccari, D., 2009).

Given this context, optimizing fertilizer usage becomes critical for ensuring food security. Among essential nutrients, nitrogen, phosphorus, and potassium are most crucial. The availability of these nutrients was instrumental in supporting the sixfold increase in global population during the 20th century (Gordeev, A., Chernyakov, B., 2001). For instance, in China between 1975 and 1984, mineral fertilizer consumption rose from 6 to 19 million tons, leading to a grain output of 365 million tons (Mineev, V.G., Bychkova, L.A., 2003).

Uzbekistan's chemical industry is primarily focused on supporting agriculture. Companies such as Maxam-Chirchiq, Navoiyazot, and Farg'onaazot manufacture nitrogen fertilizers (e.g., ammonium nitrate, urea, ammonium sulfate), while Ammofos-Maxam, Samarkandkimyo, and the Kokand Superphosphate Plant produce phosphate-based products. The Dehqonobod Potash Plant is the main producer of potassium fertilizers.

Ammonium nitrate remains one of the most widely used nitrogen fertilizers worldwide. Global nitrogen fertilizer production capacity in 2017–2018 reached 185–187 million tons (Volkova, A.V., 2019). Despite its advantages, AN has two major drawbacks: it is hygroscopic – leading to caking – and it poses a risk of explosion (Gorbovskiy, K., Kazakov, A., Norov, A., Malyavin, A., Mikhaylichenko, A., 2017; Levin, B.V., Sokolov, A.N., 2004; Lavrov, V.V., Shvedov, K.K., 2004). These issues can be mitigated by adding stabilizers such as carbonates (e.g., limestone, dolomite), potassium salts (e.g., potassium chloride or sulfate), ammonium-based compounds (e.g., ammonium sulfate, phosphates), and inert bulking agents (e.g., gypsum, phosphogypsum) (Levin, B.V., Sokolov, A.N., 2004).

Although extensive literature exists on various AN additives, systematic studies involving sodium sulfate (mirabilite or Glauber's salt) remain limited. Considering its useful nutrient components – Na_2O and SO_3—Glauber's salt appears to be a promising additive for enhancing both physical and chemical properties of AN-based fertilizers.

Objectives of the Study:

– To investigate the feasibility of producing anti-caking AN by incorporating Glauber's salt;

– To analyze the rheological properties of AN-GS solutions depending on temperature and additive concentration;

– To assess the physicochemical properties (e.g., density, strength, solubility) of AN granules modified with Glauber's salt.

Methodology

Glauber's salt, mined at the Tumryuk site, was crushed to a particle size of less than 0.25 mm and dried before use. Commercial ammonium nitrate granules (34.5% N), produced by Maxam-Chirchiq JSC, served as the base material.

The synthesis process involved dissolving GS into molten AN at 170 °C with continuous stirring. Additive ratios ranged from 0.25% to 3.0%. Following a 1–3 hour reaction period, the modified melt was granulated and subjected to analysis. Parameters measured included chemical composition (total N, Na_2O, SO_3), granule density, mechanical strength, water solubility, and viscosity across a 40–120 °C temperature range.

The experimental data are presented in Table 1 and Figures 1 and 2.

Results and Discussion

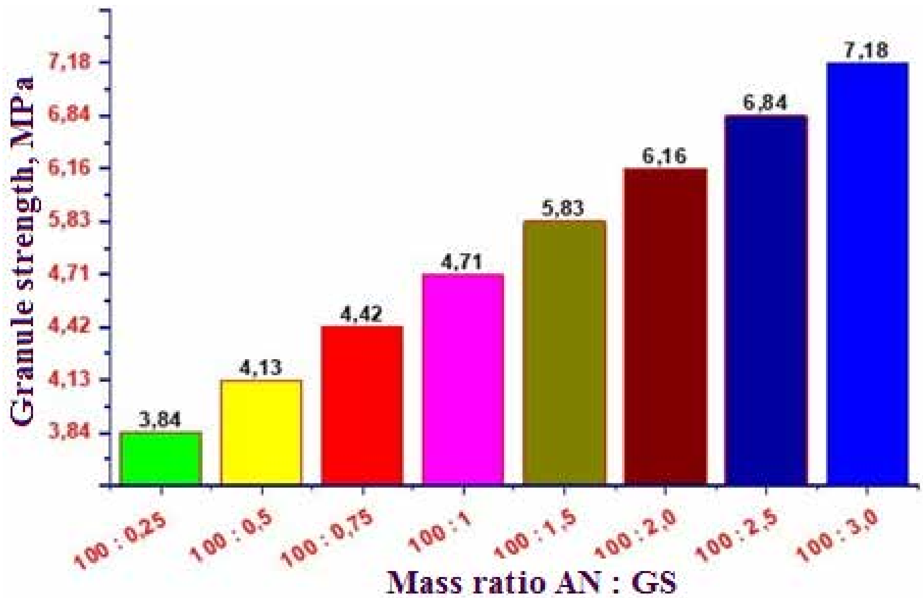
Table 1 shows that in the resulting non-caking AN, as the AN: GS mass ratio varied from 100: 0.25 to 100: 3.0, the nitrogen content decreased from 34.28% to 33.25%, while the Na_2O and total SO_3 contents increased from 0.02% to 1.11% and from 0.074% to 1.73%, respectively.

As seen in Fig. 1, the addition of Glauber's Salt (GS) to molten ammonium nitrate (AN) in amounts ranging from 0.25 to 3.0 g per 100 g of AN increases the granule strength from 3.84 to 7.18 MPa, compared to the strength of standard AN granules with 0.28% magnesite additive, which is 1.60 MPa. The increase in granule strength indicates a reduction in porosity and internal specific surface area, which in turn leads to decreased penetration of diesel fuel into the granules and consequently lowers the detonation sensitivity of the nitrate.

Table 1. *Chemical Composition of Non-Caking AN Granules Obtained by Interaction of Molten Ammonium Nitrate with Powdered Glauber's Salt*

№	Mass ratio of AN: GS	Component content, wt %				$\frac{SO_{3water}}{SO_{3total}}$,%
		N_{total}	Na_2O	SO_{3total}	SO_{3water}	
1	100: 0.25	34.28	0.02	0.074	0.070	96.48
2	100: 0.50	34.16	0.42	0.194	0.174	89.69
3	100: 0.75	34.11	0.57	0.243	0.2.13	87.80
4	100: 1.0	34.03	0.71	0.412	0.356	85.89
5	100: 1.5	33.74	0.81	0.707	0.592	84.05
6	100: 2.0	33.48	0.98	1.211	0.995	82.12
7	100: 2.5	33.34	1.02	1.613	1.293	80.16
8	100: 3.0	33.25	1.11	1.730	1.351	78.09

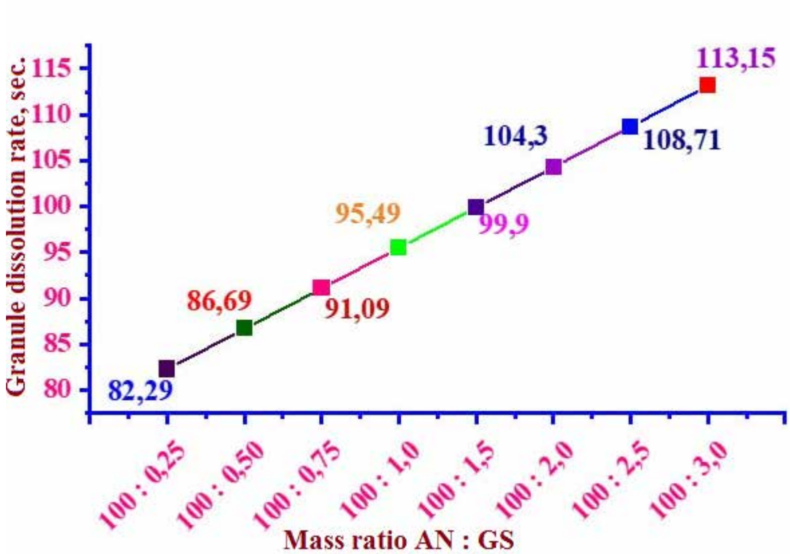
Figure 1. *Strength of non-caking AN granules containing GS*



The data in Fig. 2 show that the presence of GS in the composition of the nitrate affects the granule dissolution rate. The complete dissolution time of industrial AN granules in water averages 46.8 seconds, whereas the introduction of powdered GS in amounts from 0.25 to 3.0 g increases the dissolution time to between 82.29 and 113.15 seconds. This means that AN granules containing GS dissolve more slowly than conventional magnesian AN. Consequently, the presence of GS in the nitrate promotes a more gradual release of nitrogen from the granule.

We also determined the rheological properties of the melts of the obtained fertilizers. Density was measured using a pycnometric method, and viscosity was measured using a VPZh-2 viscometer. The experiments were conducted as follows: the nitrate samples with GS additives were melted, thoroughly mixed, cooled to room temperature, and ground into powder. The resulting powders were placed into the pycnometer and viscometer, which were then placed in a thermostat filled with glycerin. The temperature in the thermostat was raised to the desired level. The powders in the pycnometer and viscometer melted under these conditions. If the level of melt in the pycnometer did not reach the marked line, additional powder was added; if the level exceeded the mark, the excess was removed using a cotton swab attached to a wire. The temperature was controlled using a contact thermometer. The melt was held at the set temperature for 5–7 minutes, after which the measurements were taken.

Figure 2. *Dissolution rate of non-caking AN granules containing GS*



The results are presented in Table 2. As seen from Table 2, increasing the proportion of Tumryuk Glauber's Salt (GS) from 0.25 to 3.0 results in an increase in the melt density at 165 °C from 1.372 to 1.540 g/cm³ and viscosity from 9.71 to 12.31 cP. As the melt temperature increases, both the density and viscosity decrease. It should be noted that pure ammonium nitrate (AN) does not melt at 165 °C and, naturally, does not flow. However, the addition of GS lowers the melting temperature of AN. The mixture of AN with GS, at mass ratios of AN: GS from 100: 0.25 to 100: 3.0, starts to melt at 165 °C, and although the melt has high viscosity, it flows easily. The liquid state of the melts of the three-component fertilizers with GS additives in ammonium nitrate makes it possible to granulate them in a granulator.

Table 2. Rheological Properties of Non-Caking AN Containing GS

Mass Ratio of AN: GS	Density (g/cm³), at Temperature (°C)				Viscosity (cP), at Temperature (°C)			
	165	170	175	180	165	170	175	180
100: 0.25	1.372	1.363	1.355	1.337	9.71	9.88	9.44	9.13
100: 0.50	1.388	1.371	1.362	1.343	10.28	10.11	9.62	9.20
100: 0.75	1.405	1.394	1.386	1.357	10.74	10.38	9.71	9.29
100: 1.0	1.431	1.422	1.413	1.393	11.28	10.75	10.43	10.18
100: 1.5	1.450	1.438	1.430	1.409	11.61	11.34	10.87	10.72
100: 2.0	1.472	1.461	1.451	1.440	11.84	11.47	11.01	10.87
100: 2.5	1.515	1.492	1.482	1.475	12.16	11.77	11.24	11.02
100: 3.0	1.540	1.528	1.516	1.505	12.31	11.86	11.33	11.17

Conclusion

Glauber's salt is a cost-effective and agriculturally beneficial additive for modifying ammonium nitrate. Its inclusion mitigates caking, adjusts rheological behavior, and improves granule performance – offering potential for scalable fertilizer production in arid and semi-arid regions like Uzbekistan.

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