### **Research Group**



Association of independent advisers and experts in the field of mineral resources, metallurgy and chemical industry

# The CIS Calcium Chloride Market Review

Sample PDF

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#### SUMMARY

The present report expatiates upon the research of the current state of the calcium chloride market in the CIS countries and to the forecast of its development. The report will consist of 6 parts, includes 76 pages, including 20 figures and 30 tables. The given work is an armchair research. As sources of the information were used Rosstat data, the State committee of the CIS countries statistic's, Federal customs service of the Russian Federation, official statistics of rail transportation of Ministry of Railways of the Russian Federation, industry's and regional press, annual and quarterly reports, reports of negotiable papers issuers, and also Internets - sites of the enterprises - manufacturers and consumers of calcium chloride.

In the first chapter of the report presents data on existing calcium chloride "know-how", their specificities, raw materials required for the manufacture and its quality. Also in the given section there are data on the basic suppliers of raw materials (calcium carbonate and chloride-and-calcium leaches), product shipments directions and volumes.

The second chapter of the report dwells upon the manufacture of calcium chloride in the CIS countries. In the given section requirements of the existing specifications and technical documentation to calcium chloride quality are presented.

The given section of the report cites the statistical data on volumes of calcium chloride production in the CIS countries, and also in Russia (distinguishing between solid and liquid), the current state of the largest manufacturers of given production is described. At present calcium chloride manufacture is carried out only in Russia and, in a minimum quantity, in Tajikistan. In Ukraine output of the given production was stopped in 1998. In Russia calcium chloride is produced by 14 enterprises, in Tajikistan - by one. With that the share of Russia is over 99,9% of the total amount of calcium chloride manufacture in the CIS countries. For the latest 11 years calcium chloride production in Russia has grown by 61,6%.

The third chapter of the report cites the data on the foreign trade operations of Russia and Ukraine with calcium chloride for the period of 1998-1st half of 2006. In 1998-2001 foreign trade operations of Russia with calcium chloride had exportoriented character. However since 2002 due to essential increase of import calcium chloride volumes from Finland and China, the volume of import deliveries of the given production has exceeded the export volume. In the 1 half-year 2006 exportimport deliveries sharply decreased. Besides export deliveries had again exceeded import.

For Ukraine it is typical to have prevalence of import of calcium chloride over export that is caused by the absence of own manufacture of the given production in the country. The basic volume of calcium chloride is imported to the country from Russia. In the fourth chapter data on calcium chloride price level at the internal Russian market in 2002-2006 are presented, and also data on changes of the export-import prices for the given production in Russia and in Ukraine in 1999-2006 are analyzed.

In the fifth chapter of the report calcium chloride consumption in Russia is examined. In the given section the balance of manufacture - consumption of this production, branch consumption structure is presented, the current state of the basic branches consuming calcium chloride as well as the current state and prospects of development of the largest enterprises - consumers.

Consumption of calcium chloride in Russia within 1998 - 2005 2.2 times increased and had reached the level of 209,8 thousand t, in spite of the fact that in 2005 consumption of given production decreased by 12,5% in comparison with 2004.

The greatest volume of consumption of calcium chloride in Russia falls on road operation and municipal services (roads icing control) and oil-and-gas industry which share in 2005 reached 75,6%. At the same time in 2005 volume of production deliveries to the enterprises of these branches had decreased by 24,5% in comparison with 2004 and reached 158,7 thousand.

In the sixth chapter of the report the forecast of development of the Russian calcium chloride market for the period till 2010 is presented. By "Infomine" rating in the nearest years growth of manufacture of the given production in the country, caused by introduction of new capacities of calcium chloride manufacture at the existing enterprises, will be observed. According to the experts' forecast manufacture of calcium chloride in Russia by 2010 will make up 290 thousand t.

Calcium chloride consumption in Russia will depend on several factors. First of all, the appearance of alternative to calcium chloride means of roads icing control. In this case use of calcium chloride by road operation and municipal services in the nearest years will considerably decrease. Moreover calcium chloride consumption depends on the volume of oil extracted in the country. If the oil recovery is reduced, it will also lead to reduction of calcium chloride use.

According to "Infomine" forecast the total consumption of  $CaCl_2$  in Russia providing it is a favorable variant in 2010 will make 340 thousand t, a pessimistic one - 150 thousand t.

In the Addendum there are addresses and contact information of the basic enterprises producing calcium chloride in the CIS countries.

#### PREFACE

**Calcium chloride** (CaCl<sub>2</sub>) represents highly hygroscopic, easily soluble in water solid substance. The density of the compound makes up 2,512 gr/sm<sup>3</sup>. Fusing temperature of calcium chloride is 775°C, boiling temperature - 1957°C. Intensively absorbing water steam, the substance first forms solid hydrates and diffuses afterwards. Pressure of water steam on sintered CaCl<sub>2</sub> reaches 0,48 hPa. Solubility of the compound in 100 g of water makes up 49,6 g (at 0°C), 74,0 (at 200°C) and 154,0 (at 990°C). The boiling temperature of CaCl<sub>2</sub> 40,8% solutions is estimated to be at the level of 1200°C, 50% solutions - 1300°C, 75% solutions - 1750°C. Compound's water solutions freezing temperature makes up 18,57°C in case of 20% concentration and falls down to -480°C with concentration growth up to 30%. When calcium chloride solutions are being concentrated fall-out of hexahydrate which smelts at 30,1°C in crystallization water and is transformed into tetra hydrate. In the process of calcination CaCl<sub>2</sub> hydrates are partially hydrolyzed with formation of CaO and HCl.

Besides being water-soluble (with heat formation), calcium chloride could be dissolved in lower alcohols, and also in liquid ammonia with solvates formation. The solutions containing calcium chloride are received as by-products in the process of soda (ammonia method) and potassium chloride manufacture. Besides the product is got while hydrochloric acid processing in limy milk. The received solutions are steamed with formation of  $CaCl_2$  as white or grayish porous paste.

Technical calcium chloride is used in wood and wood-working, oil, oil refining and chemical industry, in refrigerating techniques, in construction and manufacturing of building materials, in nonferrous metallurgy and also for other purposes. In particular, the product finds the widest application in calcium and its alloys production, in draining of gases and liquids, acceleration of concrete hardening. CaCl<sub>2</sub> water solution is supplies a coolant, antifreeze, means against roads, air stations and railway rails icing, and also against fusion into a frozen mass of coals and ores. Besides the substance is used and in medicine as a medical product for allergic diseases and bleedings.

#### I. Calcium chloride "know-how" and raw material used in the industry

#### I.1. Ways of calcium chloride manufacture

Calcium chloride manufacture is conducted mainly at the enterprises of chemical industry. In the CIS turn out of this product is carried out in Russia, in Ukraine and in Tajikistan at the large industrial enterprises submitted in Tab. 1.

The circumstance that makes itself conspicuous is the fact that in the CIS there are no industrial facilities specializing directly in calcium chloride production. The reason for this is the fact that calcium chloride is manufactured while processing the products formed during industrial soda ash production (ammonia method), potassium chloride or electrolysis sodium chloride by recycling surpluses of chlorine or its derivatives (for example, hydrochloric acid). Solid calcium chloride is received as a result of liquid product evaporation.

Enterprise	Region	Output, thousand t/year		
THE RUSSIAN FEDERATION				
Joint-Stock company «Kirovo- Chepetsky Khimitchesky Kombinat»	Kirovo-Chepetsk, Kirovsk region	150,0		
Joint-Stock company «Caustic»	Volgograd	109,0		
Joint-Stock company «Avisma»	Berezniki, Permsky region	24,5		
Joint-Stock company «Solykamsky Magnievy Zavod»	Solikamsk, Permsky region	24,5		
Joint-Stock company «Caustic»	Sterlitamak, Bashkortostan republic	16,5		
«Soda-Chlorate» Ltd.	Berezniki, Permsky region	16,0		
Joint-Stock company «NAK «Azot»	Novomoskovsk, Tulsky region	12,5		
Joint-Stock company «Soda»	Sterlitamak, Bashkortostan republic	11,5		
Joint-Stock company «Galogen»	Perm	11,0		
Joint-Stock company «Khimitchesky Zavod Im. Karpova»	Mendeleyevsk, Tatarstan Republic	9,0		
«Volgopromkhim» Ltd.	Chapaevsk, Samara region	4,0		
Joint-Stock company «Khimprom»	Kemerovo	3,0		
Joint-Stock company «Khimprom»	Novocherkask, Chuvashia republic	2,8		

Table 1. Calcium chloride producers in the CIS countries and theirproduction capacities as per 2006 beginning

Enterprise	Region	Output, thousand t/year		
Joint-Stock company «Khimprom»	Volgograd	2,7		
Joint-Stock company «Reactive»	Angarsk, Irkutsk region	0,8		
«Usolekhimprom» Ltd.	Usole-Sibirskoe, Irkutsk region	0,3		
Total per the Russian Federation	398,1			
UKRAINE				
«Lisichanskaya Soda»	Lisichansk, Lugansk region	72,6		
Joint-Stock company «Slaviansky Sodovy Zavod»	Slaviansk, Donetsky region	47,2		
Joint-Stock company «Radical»	Kiev	10,6		
Total per Ukraine				
TAJIKISTAN				
Joint-Stock company	(Yavan settlement, Hatlonsky	0.7		
«Tadjikkhimprom»	region)	0,7		
Total per the CIS		529,2		

Source: «Infomine» research

## A. Calcium chloride manufacturing techniques out of soda ash manufacture waste products

According to industrial ammonia method of soda ash manufacturing, named also Solvay process, equimolar amounts of gaseous ammonia and carbon dioxide are run through the sated solution of sodium chloride, i.e. actually ammonium hydro carbonate is introduced into the system:

 $\frac{\mathrm{NH}_3 + \mathrm{H}_2\mathrm{O} + \mathrm{CO}_2 + \mathrm{NaCl}}{\mathrm{NH}_4\mathrm{HCO}_3} = \mathrm{NaHCO}_3 + \mathrm{NH}_4\mathrm{Cl}$ 

Sodium hydro carbonate laid-down is filtered and calcined (i.e. dehydrated) by heating, due to this in is transformed into sodium carbonate:  $2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$ 

Generated carbon dioxide and also ammonia is isolated from mother waters (at the first stage of process) according to reaction

 $2NH_4Cl + Ca (OH) 2 = CaCl_2 + 2NH_3 + 2H_2O$ 

and returned to production cycle.

Still waste liquid generated in the process containing 9,2-11,3% of CaCl<sub>2</sub>, and also 4,7-5,0% of NaCl are the by-products frequently directed to slugs. Thus it is deduced that in the process of production of 1 t of soda ash along with the given liquid more than 1 t of CaCl<sub>2</sub> and 0,5-0,6 t of NaCl are send to "tails". Evaporation

of waste liquid first leads to reception of liquid calcium chloride generally containing 32% of CaCl<sub>2</sub>, and then solid product (content of CaCl<sub>2</sub> over 90%).

The "know-how" of calcium chloride production from waste products of soda manufacture has been introduced at four enterprises of the CIS: two Russian combines - the Joint Stock Company "Soda" (Sterlitamak) and the Joint Stock Company "Soda - chlorat" (Berezniki), and also two Ukrainian plants - the Joint Stock Company «Lisichanskaya soda» (Lisichansk) and the Joint Stock Company «Slaviansky Sodovy zavod» (Slaviansk). Is should be mentioned that both Ukrainian enterprises produced both liquid and solid calcium chloride, while the Russian enterprises - only liquid (Tab. 2).

### B. Calcium chloride manufacturing in the process of potassium chlorate production techniques

Solid calcium chloride is turned out both in the process of potassium chlorate manufacture  $KClO_3$  (potassium chlorate) from remaining alkaline solution with content of  $CaCl_2$  up to 500 g/t (Fig. 1).

### Figure 1. Potassium chlorate production with calcium chloride formation flowchart



The product (hydrate) which crystallizes during the evaporation initially contains six molecules of water. Then as a result of calcinations, water gradually vanishes from the product and at temperature of  $260^{\circ}$ C waterless CaCl<sub>2</sub> is produced as solid porous paste.

Calcium chloride manufacture is organized at the Joint Stock Company "Radical" in a similar way (Kiev, Ukraine).