

## Crystallization of Ammonium-Perchlorate from Solution of Electrolytically Produced Sodium-Perchlorate in a Pilot-Scale Plant

A. Mr Živko Andrić<sup>a</sup>

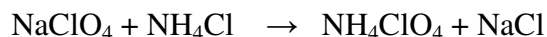
<sup>a</sup>19. December AD, Chemical process and product R&D department, 81 000 Podgorica, Montenegro

### Abstract

Large scale application of ammonium-perchlorate in the composite rocket fuels defines this compound as an important strategic material. The high content of oxygen in ammonium-perchlorate (54.5% w/w) and the fact that during the thermal decomposition does not yield solid residue, determines its application as an exceptional and irreplaceable oxidative compound in the composite rocket fuels. The fraction of ammonium-perchlorate in the composite rocket fuels is usually around 70-75% w/w, while the energetic performances of the fuel are increased even for 50% compared to the conventional fuels.

Based on these facts, and especially due to the specificity and needs of its own production process, in company "19. December" AD, Podgorica, Montenegro, is initiated production of ammonium-perchlorate on a semi-industrial scale, with original solutions for the crystallization of ammonium-perchlorate, which is a key step in production of this compound.

The core reaction in the process of crystallization is the reaction of double exchange:



First, the technological parameters of sodium-perchlorate production from sodium-chlorate by electrolytic reaction are investigated, followed by definition of key crystallization parameters in the system:  $\text{NH}_4\text{ClO}_4 - \text{NaCl} - \text{H}_2\text{O}$ . As a result of the crystallization, the product is obtained, which satisfies known and valid standards, especially from the point of granulation, crystal shape, moisture content and crystal packing density.

Keywords: ammonium-perchlorate, electrolysis, crystallization, granulation, anti-hail rockets

## 1. Introduction

Large scale application of ammonium-perchlorate in the composite rocket fuels defines this compound as an important strategic material. Improved energetic performances of these fuels compared to classical, as well as the casting technique during production of fuel elements, enable their application in space-programme rocket motors and long-range rockets missiles.

The high content of oxygen in ammonium-perchlorate (54.5% w/w) and the fact that during the thermal decomposition does not yield solid residue, determines its application as an exceptional and irreplaceable oxidative compound in the composite rocket fuels. The fraction of ammonium-perchlorate in the composite rocket fuels is usually around 70-75% w/w, while the energetic performances of the fuel are increased even up to 50% compared to the conventional fuels.

World production of ammonium-perchlorate is continuously increasing, and, although there are no precise data available at present, it is estimated in thousands of tonnes per year.

Due to the specificity and needs of its own production process (anti-hail rockets reagent) and constant problems in supply, in company "19. December" AD, Podgorica, Montenegro, is initiated research project for production of ammonium-perchlorate (APC), which resulted in installation of a semi-industrial scale plant (capacity 30 ton/year). This was preceded by a many years research work in, first, laboratory and then pilot-scale conditions.

The production on a semi-industrial or pilot scale is based on sodium-chlorate ( $\text{NaClO}_3$ ) as the basic raw material. Sodium-chlorate is submitted to electrolysis, where is converted to sodium-perchlorate ( $\text{NaClO}_4$ ), which is further, in crystallization, converted to ammonium-perchlorate ( $\text{NH}_4\text{ClO}_4$ ) in the reaction of double exchange with ammonium-chloride ( $\text{NH}_4\text{Cl}$ ).

By our knowledge, this is in the full accordance with the today world's industrial practice for production of ammonium-perchlorate.

Thus, the production of ammonium perchlorate is performed in two phases: electrolytic oxidation of sodium-chlorate to sodium perchlorate (electrolytic section), and crystallization of ammonium-perchlorate after reaction of double exchange (crystallization section).

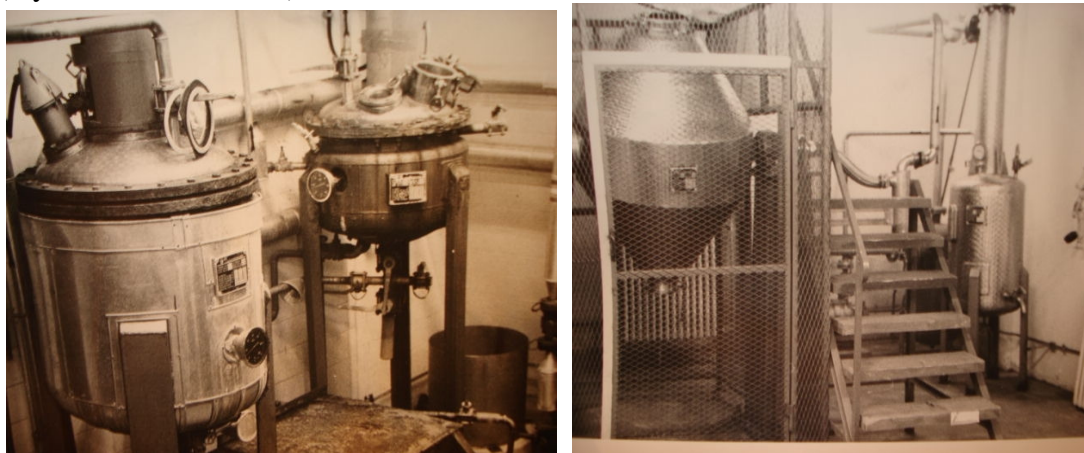
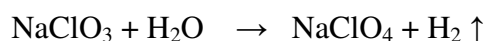


Figure 1: Pilot plant for production of ammonium-perchlorate (30 ton/year): Crystallizer and dryer

## 2. The electrolytic section of ammonium-perchlorate production facility

In the electrolytic section of the ammonium-perchlorate production facility, the sum reaction of sodium-chlorate oxidation to sodium-perchlorate is given with:



which is the basic reaction of perchlorate electrolysis.

Reaction of anodic oxidation of chlorate to perchlorate is possible only at high values of electrode potential (2-2.5 V). The standard electrode potential for equilibrium  $\text{ClO}_4^-/\text{ClO}_3^-$  is 1.19 V, while the standard electrode potential of oxygen electrode is around 0.8 V. Thus, it is obvious that two reactions will occur on anode: 1. oxidation of water to oxygen, and 2. oxidation of chlorate to perchlorate.

Consequently, it is necessary to determine the current in dependence from several parameters, which are common for these and similar systems, such as anode current density, concentration of salts in electrolyte ( $\text{NaClO}_3$ ,  $\text{NaCl}$ ), presence of additives, temperature and pH of electrolyte.

After detail analysis of these dependences, the electrolysis section of the plant is designed and installed, as shown on scheme below:

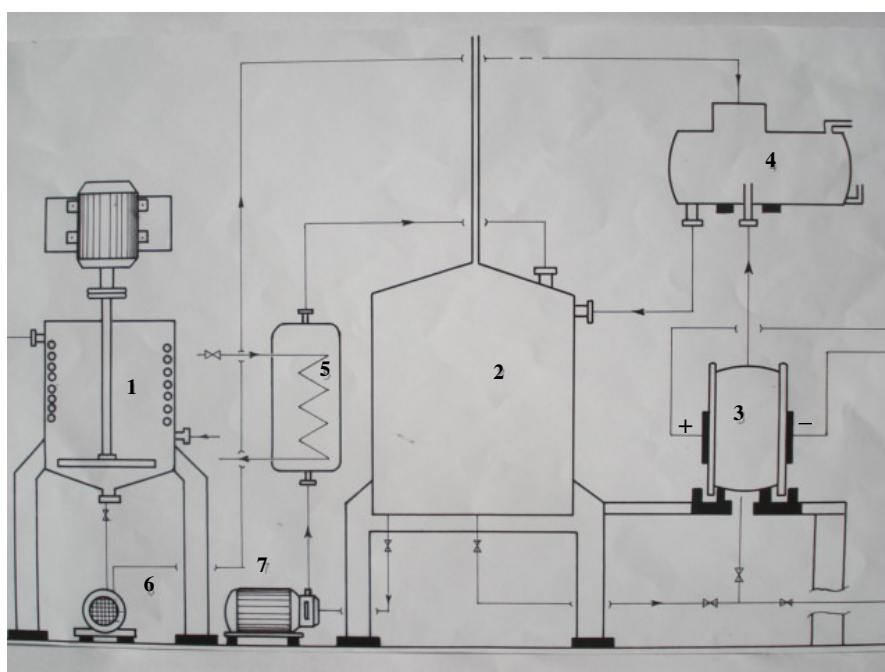


Figure 1: Electrolytic section of the plant: 1. Vessel for electrolyte preparation; 2. Collection reservoir; 3. Electrolytic cell; 4. Gas separator; 5. Cooler; 6. Dosing pump; 7. Circulation pump

The electrolytic cell is the central part of production of ammonium-perchlorate, where the chlorate is oxidized to perchlorate on platinum anode. The electrolytic cell is of "filled" type (e.g. without the gas space), which excludes the possibility of explosion. It is constructed on such a way, that anode and cathode set can be easily installed from its lateral sides, using the "comb" system.

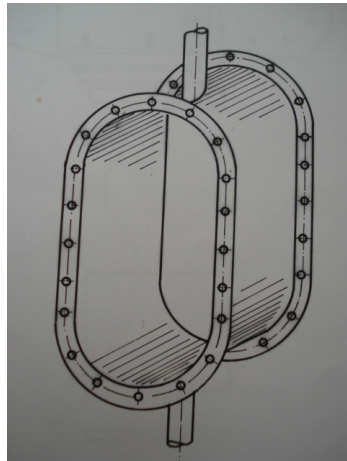


Figure 2: The electrolytic cell housing

The anode set is composed of smooth platinum leaves, welded on a platinum support (carrier), on a distance that guarantees simple installation of cathode set from the opposite side, and which ensures the minimal distance anode-cathode, and thus, the acceptable voltage drop in electrolysis. The later is in direct relation to the electricity efficiency.

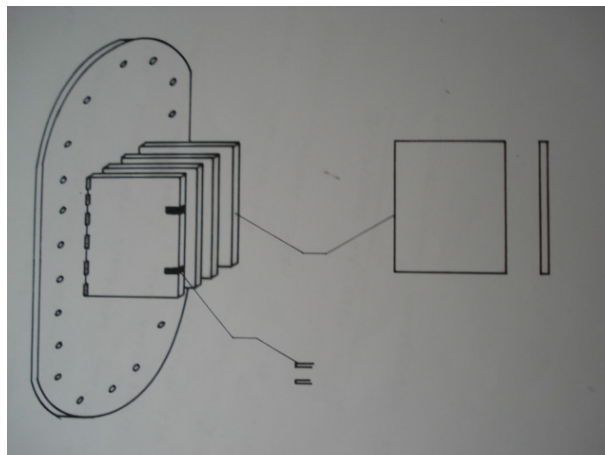


Figure 3: The anode set in the electrolytic cell

The cathode set is made by the same system, except that stainless steel is used instead of platinum. The gas separator provides constant "fullness" of the electrolytic cell and continuous discharge of hydrogen from electrolysis. The collection reservoir enables connection with the electrolytic cell and the gas separator, thus generating a unity of the electrolytic system. The constant temperature regime is maintained by the removal of heat by water cooler.

### 3. Electrolysis working regime

The validation of the technological parameters is performed on the above described section of the semi-industrial scale plant. In order to perform the electrolysis correctly, it is necessary to maintain the main parameters in defined ranges. Below are presented the values of some of the parameters in our system.

The cell current-voltage characteristics are investigated at  $T=35^{\circ}\text{C}$  and  $\text{pH} = 6.5$ , with the electrolyte composed of:  $0.550 \text{ kg/dm}^3 \text{ NaClO}_3$ ,  $0.100 \text{ kg/dm}^3 \text{ NaClO}_4$  and  $0.003 \text{ kg/dm}^3 \text{ Na}_2\text{Cr}_2\text{O}_7$ .

The cell-voltage characteristics are presented on Figure 4. The results shown below are typical that are obtained in our system.

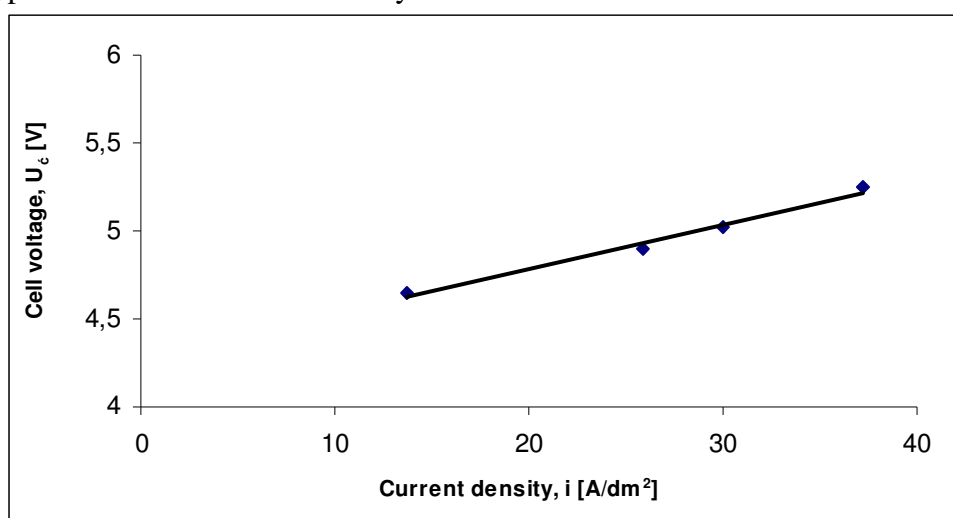


Figure 4: Dependence of cell voltage ( $U_c$ ) from current density ( $i$ )

The aqueous solution of sodium-chlorate is the electrolyte with average concentration  $1 \text{ kg NaClO}_3/\text{kgH}_2\text{O}$  ( $\sim 0.7 \text{ kg NaClO}_3/\text{dm}^3$ ,  $\rho=1.42 \text{ kg/dm}^3$ ). For the inhibition of the reduction of chlorate and perchlorate on cathode, sodium-dichromate is added to the electrolyte in concentration of  $3 \text{ g/dm}^3$ . In this system, dichromate also acts as a buffer.

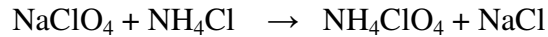
With respect to pH, electrolysis is usually conducted at 6.5, and eventual deviations from this value are adjusted with the addition of HCl or NaOH. Moreover, electrolysis is conducted at temperature interval  $35\text{-}40^{\circ}\text{C}$ , which is enabled by water cooling.

Finally, the mixing of the electrolyte is performed with the forced circulation (centrifugal pumps). In the electrolytic system, the mixing is enhanced also with so called "lifting effect", which is dependant on hydrogen release on the cathode. This enables sufficient electrolyte flow rates, even without use of the circulation pump.

The electrolytic system works stable in the defined regime, with the cell current-voltage characteristics that enable cumulative electricity efficiency of 90 %, which is close to the maximal value that are achievable with these systems. The system otherwise operates at  $2.6 \text{ KA/m}^2$ , with the current  $I=1300 \text{ A}$ .

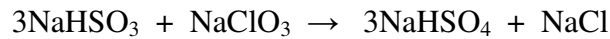
#### 4. The crystallization section of ammonium-perchlorate production facility

As said earlier, the synthesis of ammonium-perchlorate is done in two phases: 1. electrochemical synthesis of  $\text{NaClO}_4$  from  $\text{NaClO}_3$ , and 2. conversion of  $\text{NaClO}_4$  in  $\text{NH}_4\text{ClO}_4$  according to:



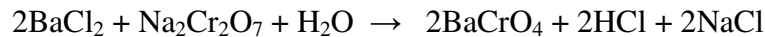
Thus, the reaction of double exchange yields  $\text{NH}_4\text{ClO}_4$  and  $\text{NaCl}$ , which need to be separated in the crystallization step.

Before submitting to crystallization, the electrolytic solution is necessary to purify. The residual chlorate is eliminated by reduction with sodium-bisulphite ( $\text{NaHSO}_3$ ):



The obtained sulphate precipitated as insoluble  $\text{BaSO}_4$  using reaction with  $\text{BaCl}_2$ , while  $\text{NaCl}$  is left in the solution.

The sodium bi-chromate ( $\text{Na}_2\text{Cr}_2\text{O}_7$ ) is eliminated by precipitating with  $\text{BaCl}_2$  according to:



The obtained  $\text{BaCrO}_4$  is separated from solution, after sufficient residence time, by decantation.

By performing all these steps, the solution is purified and can be directed to the crystallization.

The conditions of crystallization in system  $\text{NH}_4\text{ClO}_4$ -  $\text{NaCl}$ -  $\text{H}_2\text{O}$  are given on Figure 5 in a short version, which is also valid for both temperature and hydrodynamic regimes. This is because they all together create complete and unique technological design solution for crystallization of ammonium-perchlorate, which is the property of company "19. December" AD, Podgorica, Montenegro.

Crystallization of Ammonium-Perchlorate from Solution of Electrolytically Produced Sodium-Perchlorate in a Pilot- Scale Plant

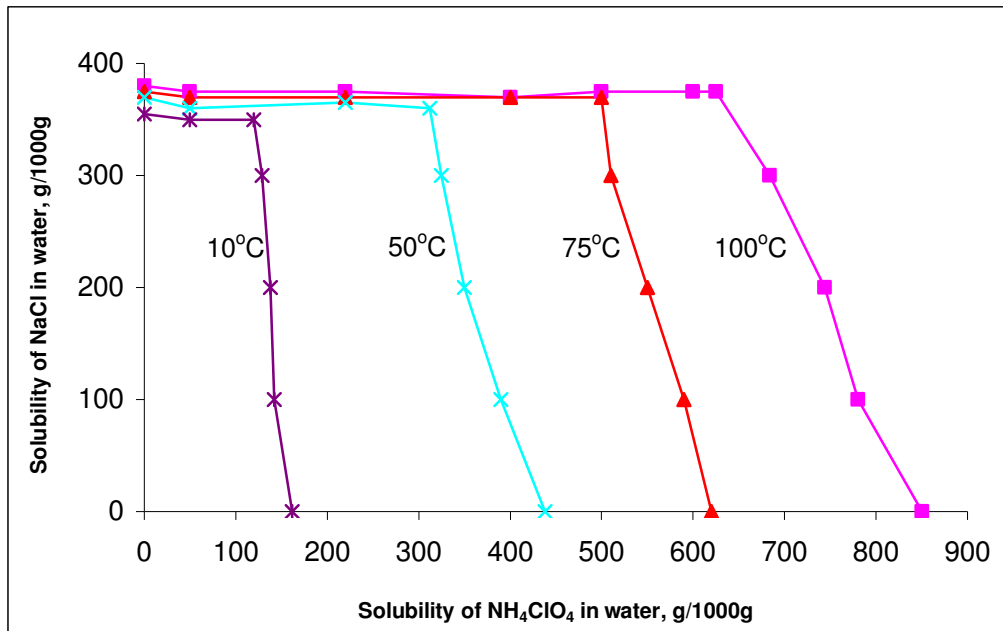


Figure 5: Experimental data for the joint solubility of  $\text{NH}_4\text{ClO}_4$  and NaCl in water

The process equipment used in this section of the facility is typical and it is not needed to describe it in more detail.

The scheme of the crystallization section of the facility is given in Figure 6:

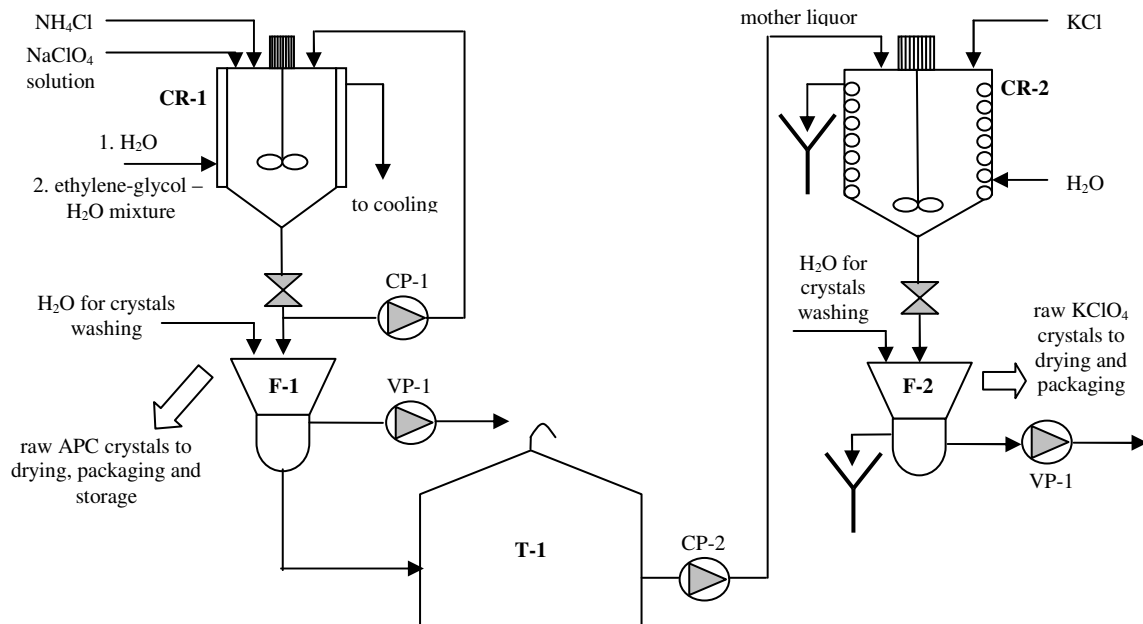


Figure 6: Crystallization section of the plant: CR-1-ammonium-perchlorate (APC) crystallizer: CR-2-potassium-perchlorate (KPC) crystallizer, F-1-Netzsch filter for separation of APC crystals: F-2-Netzsch filter for separation of KPC crystals; T-1: Mother liquor tank; CP-1, CP-2-centrifugal pumps: VP-1-vacuum pump

Crystallization is performed on such a way that the purified and heated electrolyte solution is mixed with the solution of  $\text{NH}_4\text{Cl}$ . Concentration of  $\text{NH}_4\text{Cl}$  is adjusted to give, after mixing the two solutions in crystallizer, the initial temperature of crystallization from 80-82°C.

Due to the very rigorous requirements for crystalline ammonium-perchlorate in respect to the chemical composition, moisture and crystal packing density, this crystallization is necessary to perform under strictly defined temperature and hydrodynamic regime.

With respect to temperature regime, it is primarily needed to maintain the supersaturations which are in accordance with supersaturation's consumption through the crystal growth, and not on nucleation. Thus, it is obvious that it is necessary to cool as slow as possible in the beginning of the crystallization, and with the advance in the process increase the rate of cooling.

Hydrodynamic regime in crystallization is defined with the geometry of the vessel, speed of rotation of the stirring device, the shape of the stirring device and the quality of the circulation pump, which ensures the necessary number of the crystallizer content exchanges. This regime is established to ensure the production of the crystals of spherical form (without the ledges, angles and kinks), with the required characteristics (i.e. crystal packing density).

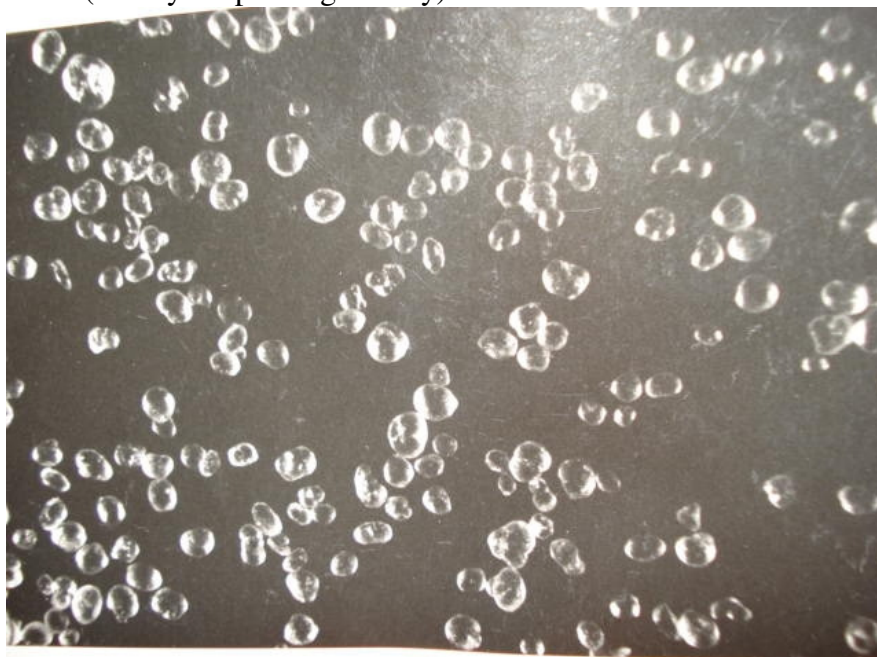


Figure 7: Ammonium-perchlorate crystals (standard 200  $\mu$ -fraction)

The cooling of the suspension in the crystallizer is done in two stages: 1. in the interval from 80-40 °C, with the water as the cooling medium, and 2. in interval from 40-10 °C, with the ethylene-glycol-water mixture.

When the cooling is terminated, the suspension is filtrated in Netzsch filter, while the raw crystals of ammonium-perchlorate are transferred to the rotating vacuum drier, where are dried at 110 °C. The dried crystals are packed in bags with added silica-gel and stored at temperature 35-40 °C, for, at least, seven days.



The obtained product has relatively homogeneous granulometric composition, which is shown in Figure 8, for ten consecutive standard 200  $\mu$ - batches:

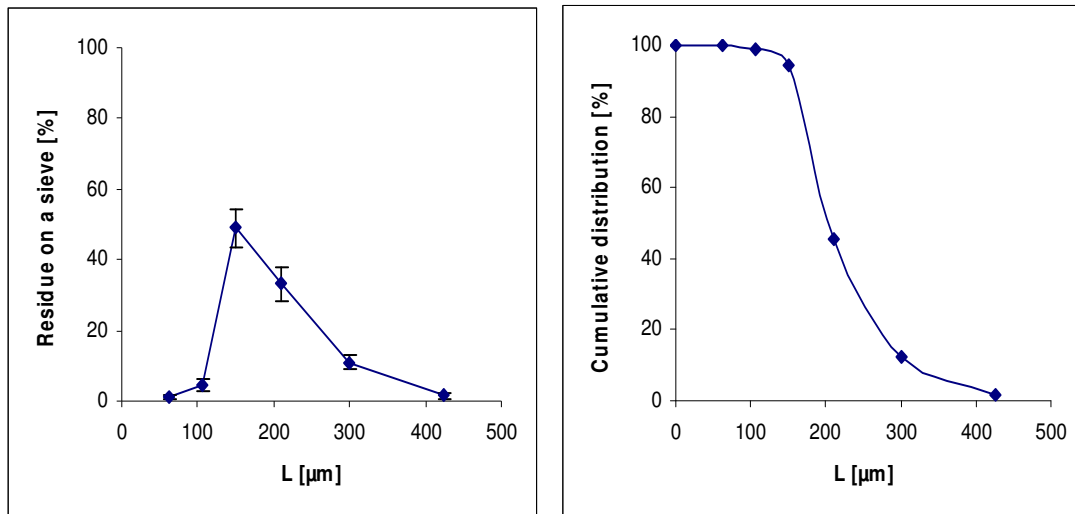
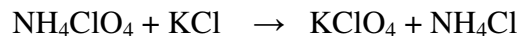


Figure 8: Granulometric composition of ammonium-perchlorate

$$(L_{50} = 200 \mu\text{m}, C_v = \frac{L_{16} - L_{84}}{2 \cdot L_{50}} = \frac{270 - 170}{2 \cdot 200} = 25\%)$$

To construct Figure 8, we have used sieves with diameters of the opening (in  $\mu\text{m}$ ): 425, 300, 210, 150, 106, 63 and "bottom". The moisture is determined using the standard Karl-Fisher method, and for the standard 200  $\mu$ -fraction is in the limits 0.04-0.07 %, while for the standard 400  $\mu$ -fraction, this value is between 0.07-0.1 %.

Finally, the mother liquor solution, left behind after filtration of  $\text{NH}_4\text{ClO}_4$ , is used for precipitation of potassium-perchlorate ( $\text{KClO}_4$ ), since it contains 100-110  $\text{g}/\text{dm}^3$  of ammonium-perchlorate:



The obtained  $\text{KClO}_4$  is separated in Netzsch filter, washed with cold water, dried at 110 °C, packed and stored.

## 5. Conclusion

The described facility is now for several years in full operation with the previously described parameters. The obtained ammonium-perchlorate is mostly spent by the producers of the anti-hail rockets, where the perchlorate is used for the production of both the anti-hail reagent (in average 50 % of APC in the pyrotechnical mixture) and propulsion composite fuel, which is installed into rocket motor of the anti-hail rocket. The quality of ammonium-perchlorate in both cases fully satisfies required conditions and yields fine results in the application.

Our several-years experience in the production of perchlorates in this facility, is based on the large number of performed experiments and connected results. During 2004, the facility is reconstructed and significant change in the main parameters is made, especially in the crystallization. The complete attempt resulted in the new quality of the ammonium-perchlorate, and this time with such characteristics, that guarantee its application, even in other programmes.

The final result of the whole experience with this facility is implemented in the new project of installation of modern factory for production of ammonium-perchlorate, with capacity of 500 ton/year, with full automation and process control, which realisation will be considered after the market and financial analysis.

## References

Schumacher J.C., *Perchlorates*, Reinhold Publishing Corporation, New York, Chapman and Hall, Ltd., London, (1960)

Jančić S.J., Grootsholten P.A.M., *Industrial Crystallization*, Delft University Press, Delft, D. Reidel Publishing Company, Dordrecht, Holand, (1984)

Jakimenko L.M., *Proizvodstvo hlora, kaustičeskoj sodi i neorganiceskih hlorproduktov*, Himija, (1974)

Matusevich L.N, *Kristalizacija iz rastvorov v hemiceskoj promisljenosti*, Himija, (1968)

Nyvtl J., Söhnel O., Matuchova M., Brovl M., *The kinetics of industrial crystallization*, Academia Praha, (1985)

Hamski E.V., *Kristalizacija v hemiceskoj promisljenosti*, Himija, (1979)

Kasatkin A.G., *Osnovnie procesi i aparati hemiceskoj tehnologii*, Goshimizdat, (1960)

Coulson, J.M., Richardson J.F., Sinnott R.K., *Chemical Engineering*, Volume 6, Pergamon Press, (1983)

Crystallization of Ammonium-Perchlorate from Solution of Electrolytically Produced Sodium-Perchlorate in a Pilot- Scale Plant

Planovski A. N., Ramm V.M., Kagan S.Z., *Procesi i aparati hemiceskoj tehnologii, himija*, (1967)

Romankov P.G., Kurockina M.I., Moszerin N.N., *Procesi i aparati hemiceskoj promisljenosti*, Himija, (1989)

Jakimenko L.M., Pasmanik M.I., *Spravocnik po proizvodstvu hlora, kausticeskoj sodi i osnovnih hlorproduktov*, Himija, (1976)

Perry R.H., Green D., *Chemical Engineers Handbook*, 6-th edition, McGraw-Hill international editions, (1984)