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#### PERCHLORATE IN THE ENVIRONMENT: NATURAL OCCURRENCE

*Physicochemical transformations on the alkali-halides crystals surface by the high-energy irradiation and cold air plasma influence were studied. The formation of the new compounds such as  $MeNO_3$ ,  $MeNO_2$ ,  $MeHalO_3$ ,  $MeHalO_4$  was set up by the IR-spectroscopy. Knowing all chain of the processes resulting in heterogeneous reactions alkali-halide crystals/atmospheric air, it is possible to try to optimize parameters of atmospheric heterogeneous reactions alkali-halide aerosol particles.*

**Keywords:** marine aerosol, particles of sea salt, alkali-halides crystals, plasma, heterogeneous reaction.

Perchlorate is an inorganic anion, consisting of four atoms of oxygen and one atom of chlorine, and is released in the environment when the highly soluble perchlorate salts,

such as ammonium perchlorate are dissolved in water. Perchlorate is not easily degraded, since the chemical reaction by which the perchlorate anion is reduced to chloride

anion has a high activation energy. Perchlorate does not bind well to other matter such as mineral surfaces or activated carbon. Due to these factors, perchlorate can persist for decades and move freely within the bodies of water. Perchlorate is a man made chemical but is also naturally occurring. Widespread perchlorate contamination in the United States was observed after the spring of 1997 when an analytical method was developed, able to detect perchlorate levels in water as low as 4 parts per billion (ppb) [1].

The presence of perchlorate in drinking water systems is mostly attributable to anthropological (man made) sources, namely activities associated with rocket fuel manufacturing or testing, and military operations. An interactive map with known perchlorate releases nationwide can be viewed on website [2]. Sites with more serious contamination levels include Lake Mead, Nevada, and the Colorado River, which supplies drinking water to more than half of Southern California, as well as Arizona and Nevada. Although the testing continues, it is believed that perchlorate may exist wherever rockets or rocket fuel were made or tested [3]. Perchlorate is present in more than 399 drinking water sources and primarily wells, and mostly those located in the counties of Los Angeles, San Bernardino and Riverside [4].

In Europe and other parts of the world, some perchlorate salts are still used for the diagnosis and treatment of some thyroid conditions.

Natural sources. Chile possesses caliche ores which are rich in sodium nitrate deposits. The sodium nitrate deposits are known to also contain naturally occurring perchlorate. The caliche is mined and leached to obtain the sodium nitrate, which is further refined to produce a commercial fertilizer. The fertilizer derived from Chilean caliche is generally marketed to growers of tobacco, citrus fruit, cotton and some vegetable crops.

It is not clear how much perchlorate is contained in caliche ores. Sodium nitrate fertilizer derived from Chilean caliche contains perchlorate at a ratio of approximately 0.5 to 2 milligram per gram [5]. It is general-

ly accepted that the process of formation of perchlorate in Chilean caliche was natural. Some evidence points to the fact that perchlorate may be generated naturally in the atmosphere, or produce by surface oxidation [6]. Natural processes for formation of perchlorate are believed to be at play in some areas, where the occurrence of perchlorate could not be attributed to any anthropological sources. Since the potential for perchlorate impacts began receiving attention in the 1990s. The USGS (U.S. Geological Survey) has undertaken various analytical studies of samples from likely perchlorate containing geological formations in the southwestern United States. These include playas, caliche-containing soils, dry lakebeds, and evaporite deposits. Evaporites minerals are those formed by evaporation concentration in arid environments. It appears that arid environments with little rainfall and high saline and mineral concentrations are conducive to perchlorate formation [7]. Therefore, it is believed that some perchlorate may also be generated by natural processes, under certain conditions, although the exact mechanism is still largely unknown [8].

Anthropogenic sources. Most of the perchlorate contamination is attributed to the use of ammonium perchlorate as an oxidizer and primary ingredient in solid rocket fuel. The majority of sites where perchlorate was detected as a contaminant in groundwater are associated with the manufacturing or testing of solid rocket fuel and with the manufacture of ammonium perchlorate [9].

Ammonium perchlorate is manufactured by the electrolysis of sodium chloride dissolved in water. Sodium chlorate ( $\text{NaClO}_3$ ) is formed as an intermediate chemical product, followed by sodium perchlorate ( $\text{NaClO}_4$ ). Sodium perchlorate is subsequently reacted with ammonium chloride ( $\text{NH}_4\text{Cl}$ ) to form ammonium perchlorate ( $\text{NH}_4\text{ClO}_4$ ). Ammonium perchlorate is further processed to make rocket fuel. The large scale production of perchlorate began in the US in the 1940s. The defense and aerospace industries purchase of more than 90 percent of all perchlorate manufactured. The approximate

percentages of perchlorate sold for specific uses are believed to be approximately 90 percent for oxidizer use, 7 percent for explosive use, and 1 percent for other uses, mostly pyrotechnics. Perchlorate typically counts for over 65 percent of the fuel in certain missiles, and nearly 70 percent of the solid propellant aboard the space shuttle. It has developed a prioritization for perchlorate impacts to drinking water. Many locations have been contaminated by the production, testing, use, and disposal of conventional military munitions such as missiles and rockets, explosives, pyrotechnics, and flares. Activities identified in this guidance which may have contributed to perchlorate releases include the:

- manufacture and maintenance of solid fuel for missiles and rockets;
- manufacture of munitions;
- use of munitions for training or testing purposes;
- munitions demilitarization;
- flare disposal;
- munitions disposal;
- use of pyrotechnics;
- open burning/open detonation operations for disposal of perchlorate materials;
- dye marker disposal as an impurity;
- electroplating as an impurity.

Perchlorate contamination also been suspected by other common industrial processes, including the:

- manufacture and uses of explosives, including the use of explosives for mining;
- manufacture and uses of fireworks;
- highway, railroad, and marine safety flares;
- use as the initiator component of air bag inflators;
- use as a laboratory reagent in chemical studies.

The world tendency of detection of manufacture of gaseous halogens in connection with research of a cycle of ozone stimulates search of new, more effective methods of generation in atmospheric air halogen containing gaseous substances. On the foreground questions of detailed studying of heterogeneous reactions alkali-halide aerosol

particles in an atmosphere are put forward. Alkali-halide particles in a plenty are submitted in structure of salt atmospheric aerosol as which basic source the surface of World Ocean serves.

The majority of reactions which are investigated in laboratories are reactions with nitric acid and oxides of nitrogen which have an industrial origin. Thus superfluous concentration of nitric acid and oxides of nitrogen are set in structure of atmospheric air. Hence, manufacture of nitrates and gaseous halogen containing substances is investigation of increase in concentration pollutant atmospheric air connections of nitrogen.

However effects of generation of gaseous halogens and nitrates are registered in natural researches the regions of an atmosphere not polluted with industrial sources. Interpretation of similar effects now is inconvenient. Therefore additional researches of heterogeneous reactions with participation alkali-halide aerosol particles are necessary.

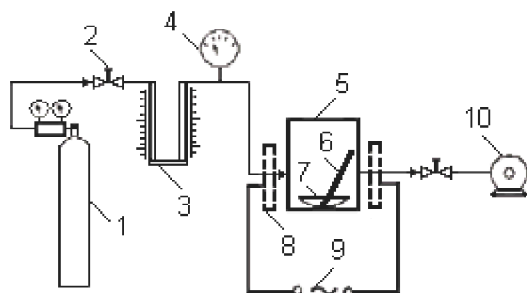
On heterogeneous reactions alkali-halide crystals in an atmosphere except for chemical pollution can operate and physical factors. It is known, that for an atmosphere the storm activity accompanying with lightning discharges is characteristic, and also presence of radioactive substances, the majority from which is transferred by aerosol not radioactive particles.

The given work has been directed on definition of a chain of the physical processes resulting in heterogeneous reactions alkali-halide crystals/atmospheric air at irradiated with x, gamma-rays or cold air plasma. For this purpose the analysis of processes, characteristic for heterogeneous reactions has been lead. Thus, knowing all chain of the processes resulting in heterogeneous reactions alkali-halide crystals/atmospheric air, it is possible to try to optimize parameters of atmospheric heterogeneous reactions alkali-halide aerosol particles with the purpose of interpretation of field measurements.

Nitrate and perchlorate are common co-contaminants in urban settings. Both ions are mobile in groundwater, moving quickly

from the source of contamination. Perchlorate was found in nearly all samples analyzed in this study. Concentrations of some samples are a concern for groundwater quality. What is clear is that perchlorate contamination is likely widespread and more research is needed in understanding non-point source pollution in addition to a clear understanding of health impacts. The goal of this research is to identify likely sources of these ions in atmosphere.

The micro crystals as powders are obtained by a method of mechanical grind. The size of particles thus made 5-10 microns. The samples in the form of powder, obtained by grinding of the alkali-halides crystals, were exposed to cold plasma, shown on fig. 1.



**Fig. 1. Reactor for generating cold plasma:**

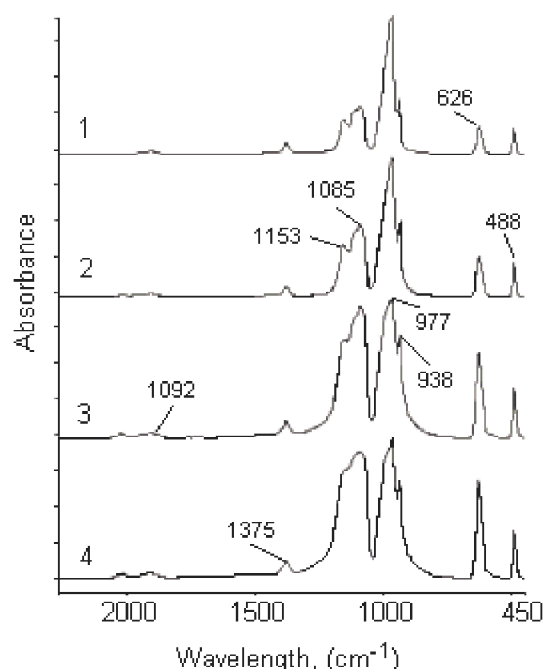
1 – cylinder with gas; 2 – vacuum crane; 3 – flow meter; 4 – vacuum meter; 5 – reactor; 6 – thermocouple; 7 – sample; 8 – electrodes; 9 – generator; 10 – for vacuum pump.

The optical properties crystals were studied after high-energy processing. The measuring was carried out on spectrometer UR-20 and spectrometer with the Fourier by transformation of firm Perkin-Elmer in a gamut 400-3000  $\text{cm}^{-1}$ .

The mechanism of the plasma chemical interaction of alkali-halides crystals shows that the formation and crystallization of such compounds as  $\text{MeXO}_4$ ,  $\text{MeNO}_3$  was observed in this case. Fine crystals, obtained by approximate grinding the alkali-halides crystals, were treated. It was shown that the treatment by the cold air plasma above 30 minutes results in the samples weight being increased as well as in the morphological changes in the samples. The morphological

changes consist in that the initial even surface of the fine crystal powder covers with crater-like formations. The particles agglomerate inside these formations. Fig. 2 shows IR spectrum for KCl after cold air plasma treatment.

The analysis of the spectrum obtained shows that the strips of absorption in areas 1300-1040, 1040-780, 670-550 and 450-520  $\text{cm}^{-1}$  correspond to vibration frequency for molecules  $\text{KClO}_4$ ,  $\text{KClO}_3$  and 1370  $\text{cm}^{-1}$ -vibration for molecules  $\text{KNO}_3$ . The alkali-halides crystals treatment in cold air plasma leads to the formation of nitrate and products with different oxidation level.



**Fig. 2. IR-spectrum KCl after cold air plasma treatment:**

1 – 5 min; 2 – 10 min; 3 – 20 min; 4 – 40 min.

Perchlorate is an anion consisting of a chlorine atom bonded to four oxygen atoms ( $\text{ClO}_4^-$ ). It is typically found in the form of perchloric acid and salts such as ammonium perchlorate, potassium perchlorate (fig. 3), and sodium perchlorate. Perchlorate is usually found as the anion component of a salt most often associated with one of the following common cations: ammonium ( $\text{NH}_4^+$ ), sodium ( $\text{Na}^+$ ), or potassium ( $\text{K}^+$ ). The resulting salts are ammonium perchlo-

rate ( $\text{NH}_4\text{ClO}_4$ ), potassium perchlorate ( $\text{KClO}_4$ ), and sodium perchlorate ( $\text{NaClO}_4$ ). Molecular chlorine and oxidised chlorine compounds (oxidation states above 0) have been observed in both the troposphere and stratosphere. Tropospheric chlorine, and halogens in general, are of interest in that they are involved in the balance of ozone production or destruction, and may drive marine boundary layer chemical processing [9]. Stratospheric chlorine chemistry is of course at the heart of the ozone depletion problem and is also closely coupled to bromine chemistry. The chlorine chemistry that produces perchlorate most likely combines multiple reaction steps involving gas-phase precursors and heterogeneous uptake of those precursors to make perchloric acid in the condensed phase.

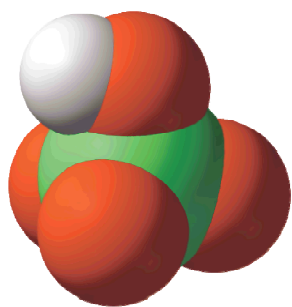
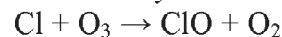


Fig. 3. Molecule potassium perchlorate.

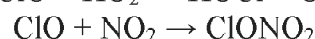
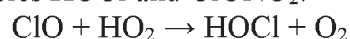
Table 1 lists the physical properties of the common perchlorate compounds. Perchlorate exhibits the characteristics of high solubility and mobility in water, as well as being very stable. These characteristics lead to the formation of long and persistent contaminant plumes when it is released into either groundwater or surface water. Like the water contaminant nitrate, perchlorate is not attenuated to any great degree by soil surface chemistry. However, it can be broken down by naturally occurring bacteria in the environment.

It was observed that  $\text{N}_2\text{O}_5$  reaction in the direct production of  $\text{Cl}_2$  [9]. These are significant sources that may account for much of the observed  $\text{Cl}_2$  and implied Cl chemistry in the mid-latitude troposphere. These active chlorine compounds,  $\text{ClNO}_2$  and  $\text{Cl}_2$ ,

are quite insoluble and photolyse readily in the gas phase to make highly reactive chlorine atoms. Chlorine atoms either react with organic compounds and are lost to the radical budget (producing HCl or organochlorides) or they react with  $\text{O}_3$  and enter into the ozone destruction cycle.



However, in the troposphere hydroperoxyl radical and nitrogen dioxide shift the active Cl and ClO species into the temporary reservoir species HOCl and  $\text{ClONO}_2$ .



Highly concentrated salt or mineral surfaces appear to be a more favourable environment for perchlorate formation in the lower atmosphere. These matrices involve high concentrations of chloride and usually nitrate.

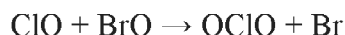
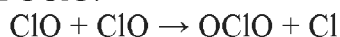
Table 1

Properties of perchlorate compounds [9]

Properties	Potassium perchlorate ( $\text{KClO}_4$ )	Sodium perchlorate ( $\text{NaClO}_4$ )
Molecular weight	138.55	122.44
Color/form	Colorless orthorhombic crystal or white crystalline powder	White orthorhombic deliquescent crystal
Taste/odor	Slightly salty	Odorless
Density/specific gravity	2.53 g/cm <sup>3</sup>	2.52 g/cm <sup>3</sup>
Solubility	15 g/L water at 25°C	2096 g/L water at 25°C
Sorption capacity	Very low	Very low
Volatility	Nonvolatile	Nonvolatile
Vapor density (air = 1)	4.8	No information
pH	6.0–8.5	7.0

Surface reactions of ozone, or the photolysis of nitrate, originally of atmospheric origin, can provide the Ox or HOx radicals required for oxidation of  $\text{Cl}^-$ . Moreover, arid high-salt environs such as the Dead Sea or Great Salt Lake have been shown to promote higher levels of gasphase XO radicals such

as ClO and BrO and may promote the formation of OCIO:



Although OCIO has not been reported in the troposphere, it has been observed in the stratosphere, and OCIO has been identified as a likely intermediate in the condensed-phase formation of perchlorate as it is known to disproportionate. The timescale for any tropospheric chemistry is constrained by the lifetime of these particles or droplets, which is at most 2 weeks. An additional source of Ox and HOx radicals could be operative in the case of minerals deposited over a period of  $10^5$  to  $10^7$  years, such as radiolysis from terrestrial radioactivity or cosmic rays.

Consider what possible tropospheric chemistry could be happening that could lead to perchlorate. Tropospheric chlorine activation is thought to involve the reaction of HO or O<sub>3</sub> with chloride-containing materials, i.e. aerosol particles, to produce either Cl atoms or molecular chlorine, Cl<sub>2</sub>; however, these processes have been unable to account for the levels of Cl<sub>2</sub> measured or deduced to be in the marine boundary layer (MBL). Recent work by our laboratory has revealed that the reaction of N<sub>2</sub>O<sub>5</sub> with aerosol-bound chloride is a source of gasphase nitryl chloride (ClNO<sub>2</sub>), a photosensitive active chlorine compound.

Stratospheric ClOx chemistry may be a more likely natural source of atmospheric perchlorate. This chemistry is driven by long-lived chloro-, chlorofluoro- and bromocarbon compounds, and takes place in a colder, dryer environment with higher UV radiation fluxes relative to the lower atmosphere. For these reasons, there are higher abundances of ClOx and BrO compounds. There are observations of particle-bound perchlorate and there is indirect evidence for perchlorate in the budget of stratospheric chlorine. Although these compounds are not stable against photolysis, a small fraction could react in the aerosol phase to form perchlorate and perchlorate, through hydrolysis and disproportionation reactions. Additional

chemistry involving the nitrogen compounds such as ClONO<sub>2</sub>, ClNO<sub>2</sub> and BrONO<sub>2</sub> could be important as those are also relatively abundant.

Volcanic sources of HCl are typically very small for the kinds of eruptions that have happened over the last century; however, mega-eruptions that have happened in the last three or four centuries might have injected significant amounts of HCl into the stratosphere rapidly enough to cause observable perturbations. The general circulation pattern in the stratosphere involves upward transport in the tropics, pole-ward transport at mid-latitudes and subsidence at the poles. This presents the possibility that snow, firn, and ice cores at both poles might contain a record of pre-industrial to industrial perchlorate formation rates, and also that perchlorate might correlate with known volcanic events if this source of HCl is significant.

As pieces of the puzzle of atmospheric perchlorate sources get filled in, there appears to be convincing evidence that chlorine radical chemistry involving ozone and/or nitrate is at the centre. The nature of these radicals (photolysis rates, solubilities) is such that the last steps in perchlorate formation almost have to be occurring in the condensed phase. It seems unlikely that typical lower atmosphere mid-latitude aerosol chemistry is sufficient to account for observed natural perchlorate because what little chlorine activation does take place seems destined to re-volatilise Cl. Also, the levels of active chlorine compounds, Cl<sub>2</sub>, HOCl, that are expected in atmospheric condensed phases (cloud droplets, aerosol particles) are quite small owing to efficient conversion of HOCl to Cl<sub>2</sub> and the low solubility of Cl<sub>2</sub>.

More rarified environments such as arid high-salt deserts or the springtime Arctic may be exceptions to the above in that they could provide conditions that promote ClO<sub>4</sub><sup>-</sup> formation, but also nitrate ion, nitrate radical, and N<sub>2</sub>O<sub>5</sub> reactions. Several observational studies could help in understanding ClO<sub>4</sub><sup>-</sup> sources. Is perchlorate present in aerosol particles and does it correlate with

different sources, or degree of photochemical processing? Are there other aerosol chemical markers for this chemistry? Process-level studies of fundamental reactions are needed and should be broadened to include not just chlorine–chlorine mechanisms (which seem unlikely given the low concentrations of these reactive species), but also nitrate ion, nitrate radical, and  $N_2O_5$  reactions. These process-level studies should focus on  $ClO_2/ClO_2^-$  reactions with  $OH/O^-$  and  $HO_2/O_2$ , which are the main products resulting from nitrate photolysis in solution and  $O_3$  uptake in aqueous solution, respectively.

In laboratory experiment the composite mechanism of interaction of salt particles with an environmental gas phase sets at action of such physical factor, as could air plasma. It, probably, is the parent reason, because of which the methods of theoretical and model calculations do not solve many aspects of transformation of a sea aerosol in a surrounding medium.

The study of the complex physicochemical process on the alkali-halides crystals surface by plasma influence is important for the solution of the fundamental problem concerned with atmospheric perchlorate formation by synthesis after cold air plasma treatment and obtaining the substances, which have an essential practical appliance.

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