Growth of nanostructures on surface of NaCl powder under gamma irradiation

E M Ibragimova, Sh N Buzrikov and M A Mussaeva

Institute of Nuclear Physics AS RUz, pos Ulugbek, 100214, Tashkent, Uzbekistan

E-mail: ibragimova@inp.uz

Abstract. The work was aimed at studying what kinds of nanostructures grow on the surface of pure NaCl powder under effect of ⁶⁰Co γ-irradiation at 140 R/s in air at 300 K, taking into account that non-irradiated surface is not perfect and may contain nanophases due to contact with wet air. Indeed, XRD has found 36±%NaCl, 16±%NaClO₃, 33±%NaOH, 14±%NaH and 1±%Na₂O, all cubic phases except orthorhombic NaOH. Energy dispersion system in SEM has confirmed deficit of Cl below the stoichiometric ratio Na/Cl. After ⁶⁰Co γ-irradiation to 10⁸ R the part of Cl-containing phases decreased to 24±% due to additional losses of Cl, while NaH phase increased up to 46±%. The following higher dose 0.7×10⁹ R caused the decrease of NaCl to 8±% (where Cl⁺) and some recovery of NaClO₃ up to 28±% (where Cl²⁺), growth of NaH to 50±% and 3±%Na hexagonal. The sizes of phases determined by Scherrer formula vary within 5-100 nm. Such mutual nanophase transformations indicate that Cl does not leave the surface and suggest nuclear reactions ⁳⁵Cl → ¹⁸O₂ + ¹⁶O₈ + ¹⁴H₁ and ⁴¹Cl → ¹¹O₈ + ¹⁵O₈ + ³¹T₁ under exposure to 1.17 and 1.33 MeV γ-quanta fluxes 2.9×10¹⁸ - 1.8×10¹⁹ cm⁻².

1. Introduction
When utilizing highly active (total ionizing 3 Gy/s) waste from nuclear energy and technologies into solid deposits, it is important to monitor the structure-phase transformations in natural rock salt due to energy absorption of radionuclide emission followed by radiolysis [1-3]. For the first time Na colloids were detected as absorption band at 565 nm developed in NaCl crystals after heavy doses >10⁸ R of ⁶⁰Co gamma-irradiation and 1.3 MeV electrons at high beam currents by W. Dale Compton [4]. Then metallic Na phase was found in NaCl powder after exposure to X-ray beam as a weak reflection [110] at 20 angle 29.5° between the main reflections of NaCl [111] at 27.3° and [200] at 31.7° [5]. Hughes suggested that a metal colloid is a large defect cluster formed by condensation of anion vacancies at dislocations [6]. Elongated Na precipitates 10-30 nm occupying volume up to 9±% were found in NaCl crystals after irradiation by 0.5 MeV electron beam in vacuum at 100 C to high doses [7]. Simultaneous actions of the direct moment transfer to different nuclear masses (²³Na and ³⁵Cl) and various ionization potentials of anions and cations unavoidably result in complicate generation of primary (Frenkel pairs) and secondary defects (anion vacancy aggregates and metal colloids). Therefore a mechanism of ionization-stimulated impact displacement is possible without certain threshold energy. The minimal energy of projectile electrons for impact displacement of Cl in NaCl was estimated within 290-320 keV [8,9]. It is much higher than the atom displacement energy due to decay of anion excitons (7.8-8.4 eV) and cation excitons (33.4 eV) [10]. Recently we first proved the influence of the growth non-stoichiometry with 5wt%Cl deficit at the polished surface (h00) of
optically pure NaCl single crystal on formation of additional nanophases of NaClO$_3$ and Na$_2$O above 80vol% due to reaction of Na with atmospheric O$_2$ and only 1v% Na nanoparticles [11]. Under $^{60}$Co $\gamma$-irradiation in air at 320 K to doses from $4\times10^5$ to $3\times10^7$ R the radiolysis of NaCl and these impurity NaClO$_3$ and Na$_2$O phases proceed with additional losses of 10w%Cl and formation of 78v% NaH phase with nanocone shape and 6v% NaOH nanofilm [11]. One should mention that grains of NaCl powder have all possible cleavage facets. Therefore phase composition of the total powder surface differs from that of the polished (h00) one.

This work was aimed at studying what kinds of nanostructures grow on the surface of pure NaCl powder under effect of $^{60}$Co gamma-irradiation, taking into account that non-irradiated facet surface is not perfect and contains equilibrium nanophases. The following tasks were put:
- What is the element and phase composition of the total cut surface of NaCl grains?
- How is it changed under $\gamma$-irradiation and does it depend on the dose?
- How much chlorine is lost from the total surface under $\gamma$-irradiation, and what dose dependence?
- Determine the sizes of observed nanophases from XRD
- Identify vibration bands related to Na-Cl, Na-Na, Na-O, Na-H, Cl-Cl, Cl-O, Cl-H from FTIR.

2. Experimental Techniques

2.1. Samples
Micro powder of NaCl of pure grade stored in dry vial, were tightly wrapped in Al foil to avoid contact with air during irradiations. Between measurements all the samples were stored in a dry hermetic box. Five portions of the same mass were prepared and one was used as a reference.

2.2. Irradiations
Samples were irradiated with $^{60}$Co $\gamma$-quanta in the dry channel at 300-320 K at the dose rate 140 R/s or flux $\sim 10^{12}$ $\gamma$/cm$^2$/s in 4$\pi$ geometry of isotropic irradiations to doses $10^5$-$10^6$ R or fluency $10^{16}$-$10^{17}$ $\gamma$/cm$^2$. The $\gamma$-quanta energies 1.17 and 1.33 MeV are more than enough for generation of electron-positron pairs [12-14]. It was found that a positron bound in the dielectric matrix annihilates slowly (from minutes to hours) with an electron bound with anion and may cause redox reactions followed by chemical reactions [14]. It means that this $\gamma$-quanta flux is capable of generating either $2.9\times10^{11}$ $e^-/cm^2$s pairs by means of absorption by Na and Cl nuclei, or $\sim 10^{12}$ Frenkel defect pairs in cm$^3$ separated at 3-5 interatomic distance by a few subsequent scattering [8,9].

2.3. Measurements
For determining the crystal structure of the subsurface layer, X-ray diffraction spectra of the reference non-irradiated and gamma-irradiated powder samples of the same mass were registered under identical conditions in the reflection mode at diffractometer XRD Empyrean (PANalytical, Netherland). Assuming presence of nanophases, Ni-filter, slits and wide angle range from 5 to 140 grad were implemented. The profile analysis was carried out with software FullProf and approaches recommended in [15]. The content of matrix and impurity phases were determined from X-ray diffraction database (PDF-2), trying the most probably compounds of Na and Cl with O and H.

As a complementary method, Fourier transformed IR-spectra were measured at spectrophotometer FTIR iS50 Nicolet (Thermo Scientific, US) with software Omnis in the attenuated total reflection mode in the wave number range 400–4000 cm$^{-1}$. The samples were compressed into semi-sphere form to ensure the best optical contact with the detector system. The observed electronic and vibration bands were identified by the IR-database and compared with the phases determined from XRD.

3. Results and Discussions
Energy dispersion system in SEM has detected some deficit of Cl below the stoichiometric ratio 39.35w%Na / 60.65w%Cl even in the non-irradiated reference sample. And after $^{60}$Co $\gamma$-irradiations this Cl deficit increased with the irradiation time and dose growth. The data for NaCl crystal and powder turned out similar [11].

4. Conclusions
...
3.1. XRD analysis

Figure 1 shows the total spectra of diffraction of NaCl both non-irradiated reference and the sample after exposure to gamma-dose $10^5$ R, when the crystal gains $F-H$ defect pairs [8-11]. It is obvious that there are at least three different cubic phases besides NaCl and some low angle (<20 grad) scattering due to amorphous nanoparticles. The observed peak profile evidences the mixture of intense narrow and weak wide reflexes corresponding to crystalline domain size 50-100 nm and nanoparticle <5 nm of the same symmetry [11,15]. The irradiations resulted mainly in redistribution of the existing peaks that is usually attributed to recrystallization, texturing, twinning. The phase composition in volume percents of the non-irradiated reference and samples irradiated to doses $10^5$ R and $0.7 \times 10^6$ R is listed in Table 1. The sizes of nanoparticles were calculated by well known Scherrer formula [15] and shown in italic under corresponding phase content.

![Figure 1. Total XRD spectra of NaCl powder: non-irradiated reference and $^{60}$Co $\gamma$-irradiated at 140 R/s in air at 300 K to dose $10^5$ R.](image)

**Table 1. Phase characteristics and composition (vol%) and crystal domain size (nm) of the non-irradiated reference and $\gamma$-irradiated NaCl powders**

| Phases, Symmetry, Group Lattice constant, nm | NaCl Cubic | NaClO$_3$ Cubic | $\alpha$-NaOH Orthorhombic | NaOH Orthorhombic | NaH Cubic | Na$_2$O Cubic | Na Hexagonal P63/mmc |
|--------------------------------------------|------------|------------------|-----------------------------|-------------------|-----------|--------------|-------------------|
| Reference, vol%                            | 36         | 16               | 33                          | -                 | 14        | 1            | -                 |
| Crystal domain size, nm                    | 101.6      | 58.5             | 98.3                        | -                 | 32.0      | 73.3         | -                 |
| $\gamma$-irradiated to $10^5$ R            | 20         | 4                | -                           | 28                | 46        | 2            | -                 |
|                                            | 105.7      | 24.7             | 78.4                        | 43.0              | 103.8     | -            | -                 |
| $\gamma$-irradiated to $0.7 \times 10^6$ R| 8          | 28               | 11                          | -                 | 50        | -            | 3                 |
|                                            | 53.8       | 53.6             | 56.8                        | 33.2              | 64.4      |              |                   |
After the irradiation to $10^5$ R the part of Cl-containing phases decreased to 24\% due to additional losses of Cl, while NaH phase increased up to 46\%. The following higher dose $0.7\times10^6$ R caused the decrease of NaCl to 8\% (where Cl\^-) and growth of NaClO\_3 up to 28\% (where Cl\^5\+), growth of NaH to 50\% and 3\%Na hexagonal. It confirms the early conclusion of Compton [4], that Na colloids are generated in the presence of OH groups. More clear conclusion that both NaH nanophase and the competing NaClO\_3 phase grow at the expense of radiolysis of NaCl and NaOH phases. And pure Na appears and grows at higher doses. NaOH with low ortho-rhombic symmetry can grow as a nanocone on the surface, as could be seen in scanning probe microscope [11]. There is no direct correlation between the amount of phases and the crystalline sizes, perhaps because of recrystallization with crystal reorientation. If the sample is closed, where is so much hydrogen come from?

In order to confirm the presence of O-H and Na-H chemical bonds, we analysed FTIR spectra.

3.2. FTIR spectra

Figure 2 shows absorption spectra of NaCl, excluding the range 2200-2000 cm\(^{-1}\) of detector noise.

![Figure 2. FTIR spectra of NaCl powder: 1- non-irradiated reference, 2 – irradiated by \(^{60}\)Co \(\gamma\)-quanta at 140 R/s in air at 300 K to dose \(10^6\) R.](image)

Spectrum 1 for non-irradiated sample shows well known intensive bands at 3200-3400 and 1800-1400 cm\(^{-1}\) attributed to Na-OH [11,16], which decrease after irradiation. Besides U-centers (hydrogen ions in anion sites) at 850 cm\(^{-1}\) decreased too [9,10,16]. While Na-H and metallic Na are responsible for increasing the background due to phonon scattering at oscillating electrons and bound protons on these nanoparticle surface. These data are in accordance with phase analysis in Table 1.

Since we irradiated under the condition of closed isolated system except the incident gamma-quanta flux, the observed phase composition on the powder surfaces corresponds (satisfies) the maintained equilibrium potential of space charge. The obtained results were compared with [3,5,11] and turned out compatible.

3.3. Gamma-induced nuclear reactions

Reversible chemical transformations NaClO\_3 \(\leftrightarrow\) NaOH under \(\gamma\)-irradiation at room temperature exclude the accepted version of evaporation of Cl or O. To explain loss of Cl and generation of H the following nuclear reactions are suggested: stable Cl nucleus absorbs either 1.17 or 1.33 MeV \(\gamma\)-quant followed by branching decay: $^{35}$Cl\(^{17}\) + $\gamma$1.17 MeV \(\rightarrow\) 2($^{16}$O\(_8\))\(^*\) + $^3$T\(_1\)* and $^{37}$Cl\(^{17}\) + $\gamma$1.33 MeV \(\rightarrow\) 2($^{18}$O\(_8\))\(^*\) + $^1$H\(_1\)*, where the products are excited and react each to other to create chemical compounds. Such kind of nuclear reactions in light nuclei is described in book [14]. Since these products are volatile they leave vacancy pores, where Na atoms accumulate as suggested by [17].

Another channel was also considered above: generation of electron-positron pair bound at Cl [12-14], although it would not result in generation of O, T and H.
4. Conclusions

In order to study what is the element and phase composition on the non-irradiated surface of a pure grade NaCl powder and how it changes upon $^{60}$Co $\gamma$-irradiation, both XRD in reflection mode and FTIR in attenuated total reflection mode were used since they are sensitive to the surface. The following results were obtained and discussed:

- The non-irradiated powder surface has the deficit of Cl and impurity of O that resulted in the charge equilibrated phase composition: 36 vol%NaCl, 16%NaClO$_3$, 14%NaH, 33%NaOH.
- During the irradiation at the dose rate 140 R/s matrix NaCl, impurity NaOH and NaClO$_3$ phases are disintegrated and $>$50% NaH nano-phase grows instead. No oxygenation of Na from air was found.
- In accordance with XRD data, IR-bands responsible for Na-Cl, Cl-O$_3$, Cl-Cl bond vibrations have decreased with $\gamma$-doses.
- Reversible losses of Cl and O and generation of H are suggested to be explained by branching nuclear reactions.

The perspective researches will be aimed at developing the radiation technology for reducing Na from NaCl by irradiation with gamma-quanta of $>$1.02 MeV. The Covid-19 related issue could be studied, such as what kind of nanophases are responsible for bactericide effect of NaCl on food, if the salt does not dominate on the powder surface?

Acknowledgments

The research was carried out with financial support from the Scientific Researches Program to President Degree 4526 of 21.11.2019. Authors wish to acknowledge special work by technical staff of $^{60}$Co gamma-facility of INP AS RUz and providing FTIR spectrometer by laboratory of physics of Center for Advanced Technologies at Ministry for Innovative Development of Republics Uzbekistan.

References

[1] Abdou S M and Moharam H. 2019 J. Phys.: Conf. Ser. 1253 012036
[2] Loman J M, et al. 1982 in Scientific Basis for Nuclear Waste Management, ed. S V Topp (Amsterdam: North Holland) 4 p 433
[3] Sugonyako A V, et al. 2004 J. Phys. Condensed Matter 16 7850798
[4] Compton W D 1957 Phys. Rev. 107(5) 1271-5
[5] Fuller R G 1966 Phys. Rev. 142(2) 524–7
[6] Hughes A E 1983 Radiation Effects 74 57-76
[7] Sulyanov S N, et al. 2007 J. Phys. Condensed Matter 19 246210
[8] Pikaev A K 1987 Modern Radiation Chemistry. Vol 3 Solids and polymers. Prikladnye aspekty (Moscow: Nauka) p 448
[9] Clinard F W Jr and Hobbs L W 1986 Radiation effects in non-metals. Ch.7 in: Physics of radiation effects in crystals. ed. R A Johnson and A N Orlov (Amsterdam: Elsevier) p 388
[10] Lushchik A, et al. 2016 Low Temperature Physics 42(7) 699-704
[11] Ibragimova E M et al. 2020 Uzbek Journal of Physics 22(5) 291-301
[12] Carlson M C J 1968 PhD Thesis The effect of gamma-radiation on the conductivity of sodium chlorine (Iowa State Univ.) p
[13] Hubbell J H 2006 Radiation Physics and Chemistry 75 614-23
[14] Friedlander G N, et al. 1981 Nuclear and Radiation Chemistry (New York: Wiley & Sons) p 700
[15] Holder C F and Schaak R E 2019 ACS Nano 13(7) 7350-65
[16] Bryukvina L L et al. 2013 Journal of Surface Investigation 7(4) 617-21
[17] Dubinko V I et al. 1999 Journal of Applied Physics 86(11) 5957-60