



Alteration of clay minerals—gamma-irradiation effects on physicochemical properties

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Abstract

In the present work, the influence of gamma-irradiation (1.1 MGy, ^{60}Co) on physicochemical parameters (“crystallinity”, specific surface, cation exchange capacity, main layer charge) of various clay minerals (montmorillonite, illite and samples of the serpentine–kaolin group) were investigated. The influence of gamma-irradiation on the physicochemical properties is generally weak. A reduction of lattice iron during irradiation could be measured, which causes decreasing values of cation exchange capacity (CEC) and main layer charge of the smectites. A weak loss of “crystallinity” of kaolinite could be observed.

The results show that the structure of clay minerals is stable even at high gamma-irradiation doses.

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1. Introduction

The long-term disposal of radioactive waste represents an important and at this time, again a current problem. Special problems arise from the extremely high radiation level even for tens of years after disposal, the substantial heat generation over a long period of time and the formation of radioactive and harmful fission products with their own geochemical behaviour. The long-term containment (1000–10000 years) should prevent from radiation additional to the natural background. There are several concepts of radioactive waste containment. Clay barriers with

highly compacted bentonite play a key role in these concepts. The safety and long-term performance of underground permanent repositories rely on a combination of several engineered and geological barriers. Different processes of bentonite buffer alteration and their influence on physicochemical properties of the buffer material were described in mineralogical and geotechnical investigations related to nuclear waste disposal (e.g. Madsen, 1998; Plötze et al., 2002). Presently, the influence of high-level ionizing radiation on the crystal structure and on physicochemical properties of clay minerals is insufficiently investigated.

1.1. Radiation level

The emplacement of high-level nuclear waste in a deep geological repository will expose the environ-

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ment of the nuclear waste container to ionizing radiation. The initial surface dose rates (gamma and neutron ray) are about 2 Gy/h and drop off by an order of magnitude within 200 years. The maximum absorbed gamma-dose during the containment period (1000 years; before the container fails) was calculated with 0.7 MGy (Reed et al., 1987). After release of the radionuclides, their alpha radiation becomes more important. The alpha radiation levels depend strongly on the solubility and sorption of the radionuclides. Reed et al. (1987) estimated a total absorbed alpha dose integrated over 10000 years of about 140 MGy near the container wall.

1.2. Irradiation effects

Some effects on clays of ionizing irradiation are to be considered. The radiation field outside the canister may affect radiolysis of water with production of solvated electrons, hydrogen atoms and OH-radicals due to ionisation and excitation processes. The amounts of H₂ and of acid from dissolved nitrogen are negligibly small (0.2×10^{-3} up to 5 mol H₂ in the first 1000 years, McKinley, 1985; Reed et al., 1987). However, the species solvated electrons e_{aq}^- and H atoms are strong reducing agents, which easily reduce metal ions. Irradiation of ferruginous layer silicates with gamma-rays has been reported to induce redox-processes on lattice iron (Drago et al., 1977; Gournis et al., 2000; Plötze and Kahr, 2001).

By means of electron paramagnetic resonance spectroscopy (EPR) some types of radiation-induced paramagnetic defect centres (RID) with spectra at $g_{eff} \sim 2.0$ had been detected in the crystal structure of natural and irradiated samples of kaolinite (Clozel et al., 1994) and montmorillonite (Gournis et al., 2001; Pushkareva et al., 2002). There are centres assigned to electron holes trapped on apical oxygen ions (Si–O centres) with different orientations. The other centre which is assigned to an electron hole located at the Al–O–Al group (Al substituting Si in the tetrahedron) shows an intense hyperfine structure with ²⁷Al nuclei in the EPR spectra at 70 K. The signal intensity of centres varies for different kaolinites, which can be used for paleodose determination (Allard et al., 1994). An influence of gamma-irradiation on such properties like surface area, particle size and cation exchange capacity of kaolinite were reported by Corbett et al.

(1963). They found a weak decrease in specific surface and “crystallinity” during gamma-irradiation (dose up to 100 kGy). Well crystalline kaolinite shows an increasing “crystallinity” (increasing Hinckley index) for gamma-doses up to 2000 Gy and an again decreasing Hinckley index at higher doses. Poorly crystalline kaolinite with a low Hinckley index shows no changes. They explained these changes in the “crystallinity” with order/disorder-processes due to static displacement of the atoms in the lattice positions, which are stimulated by the gamma-irradiation. Pushkareva et al. (2002) found that gamma-irradiation catalyses the exchange of heavy isotopes of hydrogen (deuterium and tritium) and protons of structural OH-groups. Furthermore, they explained the increase of the specific surface and change of solubility of montmorillonite and palygorskite after gamma-irradiation (30 MGy) with the increase in the amount of different types of RID. The creation of RID during irradiation (84 kGy) in montmorillonite was also shown by Gournis et al. (2001). Moreover, they described a migration of small interlayer cations (such as H⁺ and Li⁺) into the vacant octahedral positions of dioctahedral montmorillonite due to the gamma-irradiation. Bonne and Heremans (1981) could not find any influences in the retardation behaviour of clays by irradiation with gamma-dose up to 100 MGy. In a recent work of Negron et al. (2002), the effect of gamma-irradiation (2 MGy) on the structure of the SWy-1 bentonite was studied using infrared spectroscopy and nuclear magnetic resonance. No change attributable to irradiation was observed.

Further radiation-induced phenomena like the generation of fission tracks, the pleochroitic haloes around inclusion of radioactive nuclides or minerals (e.g. in micas) as well as metamictization processes (e.g. in zircon) were not described for clay minerals.

2. Methods and materials

In the present work, the influence of gamma-irradiation on montmorillonite, illite and various samples of the serpentine–kaolin group were investigated (Table 1).

No mineral purification or other changes were carried out before irradiation. After air drying, the samples were packed in closed glass containers. They

Table 1
Investigated samples

Mineral	Sample	Locality	Origin
Kaolinite	KGa-1	Washington county, USA	sedimentary (CMS source clay)
	KGa-2	Warren county, USA	sedimentary (CMS source clay)
	KNak-1	Rochlitz, Germany	hydrothermal
Dickite	KDick-1	Barkly, R.S.A.	hydrothermal
	KDickP	Huaraz, Perú	hydrothermal
	KDickM	San Juanito, Chihuahua, Mexico	hydrothermal
	RoTo204	Altenberg, Germany	hydrothermal
Nacrite	KNak2	Flöha, Germany	hydrothermal
Halloysite	KHal-1	Entre-Sambre-et-Meuse, Belgium	karst formation
	KHal-2	Djebel Debar, Algeria	sedimentary
Illite	Illit-S	Sárospatak, Hungary	hydrothermal
	Illit-M	Monte Casslano, Switzerland	sedimentary, metamorphic
Montmorillonite	SWy-1	Na-Mont., Crook county, WY, USA	alteration of volcanic ash (CMS source clay)
	STx-1	Ca-Mont., Gonzales county, TX, USA	alteration of volcanic ash (CMS source clay)
	SAz-1	Ca-Mont., Cheto, Apache county, AZ, USA	alteration of volcanic ash (CMS source clay)
	Vol	Na-Mont. (bentonite Volclay), WY, USA	alteration of volcanic ash
	MX80	Na-Mont. (bentonite MX-80 new), WY, USA	alteration of volcanic ash (Süd-Chemie)

were irradiated at room temperature in a ^{60}Co gamma-source. The dose rate was 2.548 kGy/h and the integrated dose 1.1 MGy. After irradiation, the samples were stored in closed glass containers at 10 °C.

For element analytical data of the investigated clay samples, see Götze et al. (2002) and for the CMS source clays, see Mermut and Cano (2001) and Kogel and Lewis (2001).

The mineralogical composition and the crystal structure (“crystallinity” indices like Hinckley index and FWHM) of the investigated samples were characterised by X-ray diffraction (XRD) (BRUKER-

AXS D8; $\text{CuK}\alpha$, range 4–70°2 θ , step size 0.02°, counting time 3 s). Rietveld refinement with the program AutoQuan/BGMN was used for mineral quantification and for calculation of the relative proportion of the high-defect kaolinite (Plançon et al., 1989) by assumption of a two-phase model in calculation (an ordered and a disordered kaolinite). For results of phase quantification, see Götze et al. (2002) and for the CMS source clays also Chipera and Bish (2001).

For identification of point defects in the crystal structure of the clay minerals, paramagnetic centres

Table 2
Physicochemical parameters of various clay samples

Sample	BET (m ² /g)		CEC (meq/100 g)			Main layer charge (eq/mol)		
	Natural	Irradiated	Natural	Irradiated	Irradiated after 22 months	Natural	Irradiated	Irradiated after 22 months
KGa-1	7.9	7.8	<1	<1				
KGa-2	19.7	19.2	<1	<1				
KDickM	1.4	1.7						
KHal-2	62.9	62.6						
Illit-M	56.9	54.2	33	32	33			
Illit-S			21	17	18			
SAz-1	70.8	71.2	128	127	120	0.39	0.38	0.31
STx-1	68.1	65.0	92	92	87	0.33	0.32	0.30
SWy-1	22.2	22.8	85	84	81	0.28	0.28	0.23
MX80	18.2	17.8	84	85	78	0.28	0.28	0.23
Vol			88	90	86	0.29	0.28	0.24

were investigated in powder samples by electron paramagnetic resonance spectroscopy (EPR) (BRUKER ESP 300E; X-band, $T=295$ and 70 K, $H_M=0.5$ mT, $p=40$ mW, range 100 – 400 and 320 – 336 mT, $m=50$ mg).

Infrared (IR) spectroscopy as a complementary method to X-ray diffraction and other methods gives among other things unique information about the mineral structure and the degree of regularity within the structure. Samples of 2 and 0.5 mg were dispersed in 200 mg of KBr and pressed to a clear pellet. Fourier transform IR spectra were obtained in the middle-IR region (4000 – 400 cm^{-1}) with a Perkin Elmer FT-IR

2000 on KBr-pressed discs in absorption mode. For the CMS source clays, see also results in [Madejová and Komadel \(2001\)](#).

To find irradiation-induced changes in physico-chemical properties, the following parameters were studied: specific surface area, cation exchange capacity and mean layer charge. The specific surface was measured with N_2 -absorption (so-called BET surface after [Brunauer et al., 1938](#)) with a GEMINI-analyser (five-point measurements). The cation exchange capacity (CEC) of the clay minerals was determined using the complexes of copper (II) ion (0.02 M Cu (II)-triethyltetramin) after [Meier and Kahr \(1999\)](#). Mean

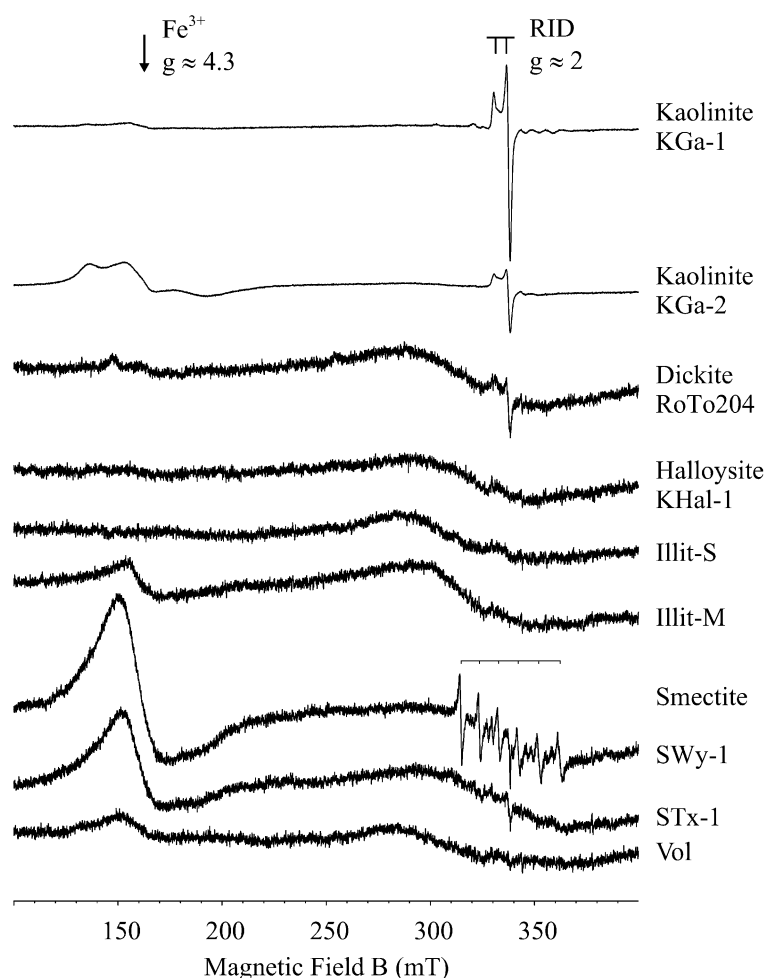


Fig. 1. EPR spectra (X band, 295 K) of natural clay samples showing the signals of RID and Fe^{3+} . The six-line hyperfine structure in SWy-1 derives from Mn^{2+} in some calcite (1.5 wt.%) in the sample ([McBride, 1995](#)). The intensity of the EPR spectra of kaolinite is divided by 10.

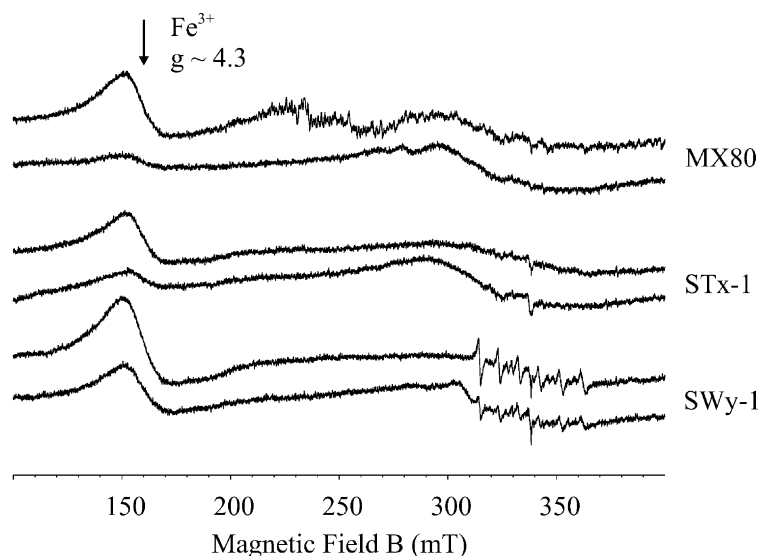


Fig. 2. EPR spectra (X band, 295 K) of smectite before (top) and after (bottom) gamma-irradiation showing the decrease in the intensity of the Fe^{3+} -signal at $g_{\text{eff}} \sim 4.3$. Note the increasing intensity of the RID-centres at $g_{\text{eff}} \sim 2$.

layer charge estimation was carried out by alkylammonium ion expansion after [Olis et al. \(1990\)](#). For the CMS source clays, see also results in [Mermut and Lagaly \(2001\)](#).

3. Results and discussion

The influence on the physicochemical properties is generally very weak ([Table 2](#)). The changes in the macroscopic characteristics as specific surface and CEC due to gamma-irradiation are irregular for the

different clays examined. Kaolinite, dickite and halloysite show no changes in the BET surface. Weak changes could be registered for illite and montmorillonite. The BET surface of illite decreases during irradiation (decrease of $2.7 \text{ m}^2/\text{g}$). The behaviour of the montmorillonite is not uniform. Only the STx-1 shows a decrease of $3.1 \text{ m}^2/\text{g}$. For the other samples SWy-1, SAz-1 and MX80 no clear changes could be seen. The variations lie mostly within the margins of error of the methods. No changes in the CEC and the main layer charge could be observed after irradiation. However, after storing for 22 months the montmorillonite samples show up to 10% lower values for the CEC and the main layer charge. These observations are in relationship to the iron content and his changes in the valence state due to irradiation. We registered the EPR signal at $g_{\text{eff}} \sim 4.3$ from Fe^{3+} ions substituting for octahedral Al^{3+} (e.g. [Meads and Malden, 1975](#); [Balan et al., 1999](#)) almost in all clay mineral

Table 3
EPR-intensity of the Fe^{3+} -signal at $g_{\text{eff}} \sim 4.3$ of various clay samples

Sample	Fe^{3+} amplitude intensity (arbitrary units)	
	Natural	Irradiated
KGa-1	900	700
KGa-2	4800	4900
RoTo204	250	250
Illit-S	50	50
Illit-M	500	300
SWy-1	2500	1400
STx-1	1500	500
SAz-1	800	800
MX80	1800	400
Vol	400	400

Table 4
“Crystallinity” parameters of kaolinite

Sample	Hinckley index	
	Natural	Irradiated
KGa-1	0.95	0.93
KGa-2	0.33	0.33
KNak-1	0.90	0.99

samples (Fig. 1). The lowest intensities were detected in the dickite and nacrite samples, whereas illite, montmorillonite and the Fe-rich kaolinite KGa-2 show the highest intensities. The very broad signal at $g_{\text{eff.}} \sim 2.0\text{--}2.4$ arise from spin–spin interactions in clusters of Fe^{3+} and other ions present as impurity phase and surface hydrated species (Goodman, 1978; Luca and Cardile, 1989). Especially in montmorillonite with a higher Fe^{3+} content, we found the signal of structural Fe^{3+} at $g_{\text{eff.}} \sim 4.3$ with strongly decreased intensity after gamma-irradiation (Fig. 2, Table 3). A possible explanation is the reduction of Fe^{3+} to Fe^{2+} (which is not viewable in EPR) due to hydrogen

atoms and solvated electrons as products of the radiolysis of the interlayer water (Drago et al., 1977; Gournis et al., 2000). The hydrogen atom can diffuse into vacant octahedral sites towards an Fe^{3+} site resulting in Fe^{2+} and H^+ . While the protons remain in the octahedral layer there are no changes in layer charge. With the time, the protons can diffuse away, which leads to lower values of layer charge and CEC.

The kaolinite samples were studied with regard to changes of “crystallinity” due to the gamma-irradiation. Only weak changes in “crystallinity” of kaolinite could be detected after irradiation (Table 4). This seems to be in contrast to the observation of

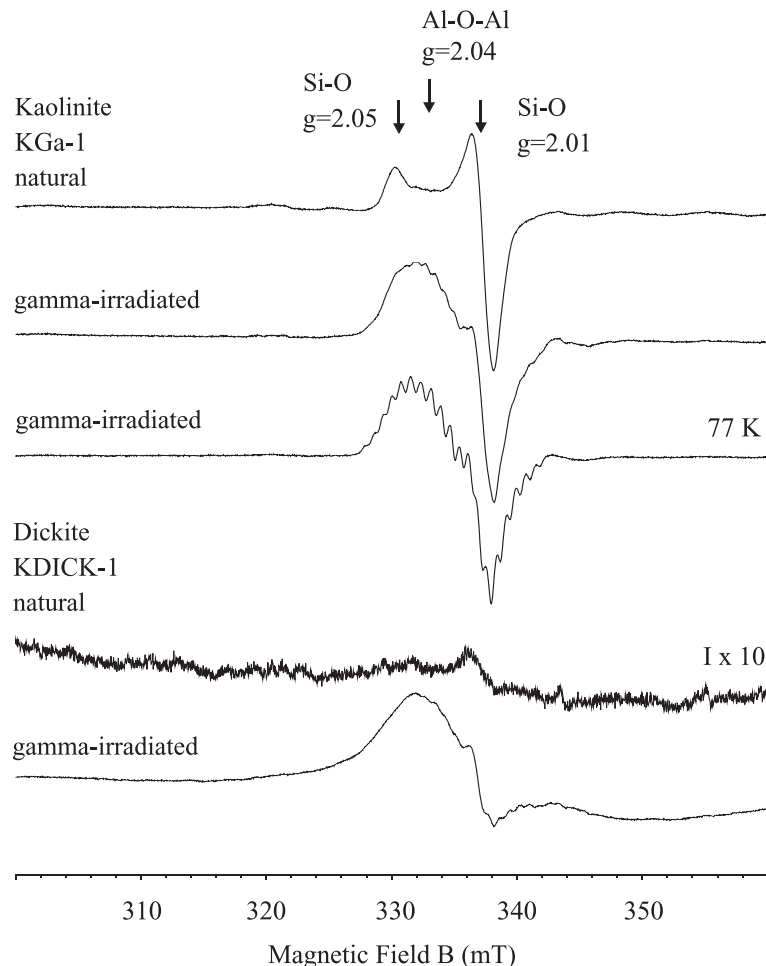


Fig. 3. EPR spectra (X band, 295 K) of kaolinite and dickite before and after gamma-irradiation showing the increase in the intensity of the radiation-induced defects centres. Note the decreasing intensity of the Si–O centre and the simultaneous increasing of Al–O–Al centre in kaolinite.

Corbett et al. (1963). However, their values for natural and highly irradiated samples show also only small differences. Because of our measurements of natural and of highly irradiated samples only, we could not observe the increasing Hinckley index at lower gamma-dose.

Clear influences of irradiation on clay minerals could be found in the spectroscopic properties but not in FT-IR. By means of EPR spectroscopy some types of paramagnetic defects had been detected in natural and irradiated samples (Fig. 1). One important group of paramagnetic centres is the mentioned radiation-induced paramagnetic defect centres (RID) with spectra at $g_{\text{eff.}} \sim 2.0$ (Clozel et al., 1994). The signal intensity of centres varies for different kaolinites. The highest concentration of RID was measured in well crystallized kaolinite. During gamma-irradiation, the intensity of RID centres strongly increases. The intensity of Al–O–Al centre increases more strongly than those of the Si–O centres (Fig. 3). In illite and montmorillonite, very weak signals of RID could be detected. However, the results of XRD and Rietveld analysis of the clay material show that all samples contain other phases. Therefore, it cannot be excluded that some signals derive from impurity phases, e.g. from small amounts of quartz, whose RID's show very similar parameters.

4. Conclusion

The influence of gamma-irradiation on the physicochemical properties of clay minerals is generally weak. The illite shows a weakly decreasing specific surface. A reduction in valence state of lattice iron during irradiation was found, which causes decreasing values of CEC and main layer charge of the smectites. A very weak loss of “crystallinity” of kaolinite could be observed. Clear influences could be found on the spectroscopic properties. Gamma-irradiation mainly causes changes in the defect structure of clay minerals. There are especially the radiation-induced defect centres in the kaolin-group minerals.

The clay mineral structure is stable even at high gamma-irradiation doses. However, the influence of the alpha-irradiation is not yet known and should be investigated for the suitability of clays in the safe disposal of radioactive waste.

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