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MEMO

FROM: Carl Boyars, Consultant

TO: K. Chang, NRC

SUBJ: Bentonite Characteristics as Packing Material or Backfill

INTRODUCTION

The organic content (humic substances) of bentonite, which is intended to comprise 25 weight percent of the packing material for high-level waste in a basalt repository, can affect the corrosion processes of the steel canister and also the transport processes of the radionuclides once the canister is breached. A search for information on the organic content of bentonite has, therefore, formed a part of the task of estimating the performance of a repository for HLW. We have been fortunate to locate an extensive review paper by R. Grauer of the Swiss Federal Institute for Reactor Research. That review (EIR-Bericht Nr. 576), entitled "Bentonite as Backfill Material in the Final Repository for High-Level Waste: Chemical Aspects" is in German, except for a two-page summary reproduced herein. I have translated from that review the introductory portions and everything that pertains to the organic matter of bentonite. In this report, I am giving either a full translation or a digest of the sections relevant to the immediate interest. Any mention of organic matter is underlined in this report. I have also taken the liberty, in translating, of correcting apparent typographical errors in the German text. The goal of this report is to provide and to lead to sources of the best data on bentonite for use in computer models of HLW repository performance. This report does not constitute a "critical review", which would have required comparison of Grauer's review with the reference material on which it is based.

Summary

The present Nagra concept for disposal of high-level waste foresees emplacing the steel containers enclosing the borosilicate glass in tunnels of 3.7 m diameter at a depth of 1000 to 1500 m. These tunnels are to be backfilled with compacted bentonite, a clay with a high montmorillonite content. Bentomites are suitable as a backfill due to, inter alia, their swelling capability, their low hydraulic conductivity and their sorption properties.

This report is restricted to those chemical aspects of the backfill material which can affect the behaviour of a repository system: svelling capability, sorption properties and long-term stability.

Under repository conditions, the svelling of montmorillonite upon vater inflow is primarily innercrystalline. At present, there is no microscopic model which gives a quantitative description of this process. However, on the basis of equilibrium thermodynamics, relationships can be deduced between svelling pressure and experimentally more easily determinable water vapoor sorption isotherms and heats of immersion.

Cation adsorption, which is important for nuclide retention in the repository, can be described by appropriate models. However, for various reasons, interpretation of published sorption data is rarely possible from a theoretical viewpoint and direct diffusion measurements on compacted bentonite are therefore preferable to the use of sorption data.

It can be concluded from natural analogue studies and from laboratory experiments that the properties of the backfill material vill not alter significantly over a period of 10⁶ years. Nevertheless in the long term, the formation of mixed-layer illite/montmorillonite cannot be ruled out. Such mixed-layer clays still have good svelling and sorption properties. Given the quantity ratios foreseen, no adverse changes due to radioactive decay are to be expected. The interactions between the bentonite and the container corrosical products must, in the absence of literature data, be investigated experimentally. The type of reaction products expected (iron-containing clay minerals) and the high bentonite/iron ratio lead to the conclusion that the function of the backfill need not be impaired by these processes.

Because of its better stability, a calcium bentonite is preferable to the sodim variant. A low iron content is desirable because, under reducing conditions, the surface charge of the montmorillonite is increased by reduction of iron (III). Organic and sulphidic contaminants should also be kept to a minimum.

GRAUER'S REVIEW

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1 THE FINAL REPOSITORY CONCEPT AND REQUIREMENTS OF THE BACKFILL MATERIAL

1.1 The final repository concept for high-level waste

The present Swiss concept for the final repository for highly radioactive wastes is fully described in the NAGRA Report on Project "Security" ("Gewachr"). The intended multiple-barrier principle is, therefore, illustrated only briefly in Figure 1.

The wastes consolidated in a borosilicate glass matrix are enclosed in a self-supported steel container that has a wall thickness of 25 cm. The container is designed for a lifetime of at least 1000 years. After this time, the concentration of both critical muclides, Sr-90 and Cs-137, is decreased to an insignificant value and the temperature in the repository has reached about 55°c, the temperature of the surroundings.

The steel containers are emplaced in host rock (granite or gneiss) at a depth of 1000 to 1500 m in a tunnel of 3.7 m diameter. These tunnels are filled with bentonite, i.e., a material with a high proportion of the clay mineral montmorillonite.

1.2 Requirements of the backfill material

The backfill material of a repository comprises an important link in the chain of security barriers that have to satisfy specific physical/ mechanical as well as chemical requirements. The most important requirements are (see also refs. 128, 133, 185, 187):

-low water permeability in comparison to the host rock

-high ability to retain radionuclides

-compatibility with the other repository components

-swelling ability for packing of interstices in metastable structures and of rock fissures

-plasticity for compensation of rock displacements and for homogeneous pressure distribution

-sufficient load-bearing capacity in order to prevent sinking of the canister

-stability over a time period of at least 10⁶ years

-sufficient availability and low cost

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This requirements profile is more or less well fulfilled by numerous substances or mixtures. Table 1 contains a selection of proposed backfill materials. A compilation of substance properties is given in ref. 105.



Abb. 1:

Das System der technischen Sicherbeitsbarrieren in einem Endlager für hochaktiven Abfall. Der Tunneldurchmesser beträgt 3,7 m (Nagra).

The hyster of technical semisting barries in a repository for high teal wate. The tunnel diameter is 3.7 m.

TABLE 1: Proposed	<u>l Backfil</u>	l Materials	for a	Repository	(25)	2

Clays

Na- and Ca-bentonite Illite

Zeolites

Clinoptilolite Synthetic products

Quartz sand

Drying agents

Metal powders and metal compounds

Activated carbon

Calcium oxide

Magnesium oxide

Minerals, Rocks

Glauconite Serpentine

Anhydrite Basalt Tuff

Pyrite

Iron Aluminum Lead oxide

Bentonite is considered as tunnel backfill material in Project "Security" ("Gewachr"). This clay corresponds very extensively to the specified requirements.

In Sweden, bentonite is also considered as a backfill material. In this connection, several reports were written; of these, the general content works are refs. 128, 129, and 133. Further works which deal completely or partially with bentonite as backfill material are refs. 103, 105, 158, and 187. Brookins (25) gives a summary of all American work. The investigations on bentonites that were carried out under the sponsorship of NAGRA are mentioned later in the text.

1.3 Goal of this work

Because mimerous publications about bentonite as backfill material already exist, it is not intended to give a summary overview once more. An overview is to be given of the important chemical aspects which determine or influence the behavior of bentonite in a final repository system. Therefore, the chief emphasis is placed on swelling behavior, sorption properties, and stability under final repository conditions. In connection with the stability, the interactions of the bentonite with the corrosion products of the container and with the glass matrix are considered in addition to the possible diagenetic reactions, as well as stability under radiation from radionuclides.

The restriction to these selected single aspects should not be allowed to mislead, for a repository presents a complex system, and the isolated observation of a single component can lead, on occasion, to an incorrect conclusion.

2 THE STRUCTURE OF CLAY MINERALS AND NATURAL BENTONITE

2.1 The structure of clay minerals

The essential component of bentonite is the clay mineral montmorillonite, whose properties have a close dependence on its structure. The structure of clay minerals is discussed here only so far as is needed for an understanding of their chemical and physical properties. A broader treatment of the structural aspects is found in the monographs (23, 63) on which the following exposition is based. The chapters "Silicates" (86) and "Clay and Clay Minerals" (85) of "Ullmanns Enzyklopaedie der technischen Chamie" give a condensed presentation.

2.1.1 Structure principles

The building blocks of the layer silicates (phyllosilicates) are SiO₄-tetrahedra (T) and MO₆-octahedra (O) in which the metal ion M is mainly aluminum or magnesium. The octahedra form strata from two layers of densely packed oxygen ions or hydroxide ions. With M = Al, only 2/3 of the octahedral positions are occupied (dioctahedral series). With M = Mg, all octahedral positions are occupied (trioctahedral series).

The T are linked with one another, with all Si atoms lying in a plane. No dense oxygen packing results with this arrangement; 6 T always surround a hexagonal void.

The great variety of phyllosilicates comes about through variable arrangements of T and O layer sequences and also through the isomorphons substitution of metal ions. Through such substitutions, the strata packets contain negative charges, which are compensated by the infiltration of cations in the space between strata. The charge density of the strata and the hydration behavior of the infiltrated cations are the essential major influences which determine the swelling and ion exchange properties of clay minerals.

2.2 Natural bentonites

There is a comprehensive monograph on bentonites (64). Vogt and Koester (175) have thoroughly investigated 19 bentonite samples chemically and mineralogically.

Bentonites (named after Fort Benton) are clays with a high swelling ability. Originally, the designation bentonite was used only for those products which arose <u>in situ</u> from a reaction of volcanic ash with water. Occasionally, the designation is used also for clays with "bentonite-like" properties which have formed through hydrothermal decomposition of volcanic rocks.

The major component of bentonites is montmorillonite; its content ranges from 65 to 99 percent. Depending on the composition of the volcanic ash and the formation conditions, bentonites contain varying proportions of quartz, mica, feldspars, and other minerals.

The space between strata in montmorillonites contains mainly calcium, often together with magnesium. Sodium-montmorillonites are rarer; typical representatives are the Wyoming bentonites. The type of exchangeable cations results from the composition of the volcanic ash; there is no correlation with the water composition. The montmorillonite of bentonites consists of extraordinarily fine particles. Most of the particles are smaller than 0,2 micrometers.

Bentonites are distributed worldwide (64), to be sure often not in deposit sizes worth mining. Wyoming bentonites have already been mentioned. Further deposits are found in South Dakota and Montana, In Bavaria are found significant occurrences of Ca-bentonites, which contain montmorillonite with large quantities of iron in the octahedral layer. The Swiss bentonite at Bischofszell is only of small size. Because of its high stratum-charge of 0.64 per 010(OH)2 unit and because of the high magnesium content, it is not ideal as a backfill material.

In connection with Project "Security" ("Gewachr"), a Na-bentonite (MX-80 from Wyoming) and a Ca-bentonite (Montigel from Bavaria) were investigated in detail (106, 107). Their mineral composition is shown in Table 3. Noteworthy is the different content of organic carbon, which could be controlling for the complexing of heavy metals.

The mineral formulas and other properties are in Table 4.

in	Percent of the Oven-Dried Samples (107)	<u></u>
Mineral	MX-80	Montigel
Montmorillonite	75	66
Quartz	15.2	8.3
Mica	under 1	12-15
Feldspars	5- 8	2-4
Carbonates	1.4	3.8
Kaolinite	under 1	2
Pyrite (FeS ₂)	0.3	0
Other Minerals	2	2-3
Organic Carbon	0.4	0.03

Table 3: Mineralogical Composition of Bentonites MX-80 and Montigel

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Table 4: Mineral Formulas and Fur	ther Data on Bentoni	tes MX-80
and Montigel		
	<u>MX-80</u>	Montigel
Montmorillonite Content	75 %	66%
Molar Mass of Montmorillonite	372.6 g	375.0 g
Bentonite Surface Area	562 m ² /g	493 m ² /g
Cation Exchange Capacity	76 meq/100 g	62 meq/100 g
Exchangeable Ions	86\$ Na ^{\$}	(61% Ca ^{2‡} (36% Mg ^{2‡}
Charge between Layers, per 010(OH)2 - Unit	0.30	0.28
Density of Bentonite	2.755 g/cm ³	2.847 g/cm ³

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Mineral Formula of Montmorillonite: MX-80: $(Si_{3.96} Al_{0.04}) (Al_{1.55} Fe_{0.20} Fe_{0.01} Mg_{0.24}) O_{10}(OH)_2 Na_{0.30}$ Montigel: $Si_{4.00} (Al_{1.36} Fe_{0.31}^{3^+} Fe_{0.01}^{2^+} Mg_{0.35}) O_{10}(OH)_2(Ca, Mg)_{0.14}$

3 CLAY/WATER SYSTEMS

3.1 Composition of water in contact with bentonite

The pH is an important parameter for the corrosion properties of steel containers and also of waste-containing glasses. In the bentonite backfill, it is not determined only through the pH value of the site water. Solution equilibria, possible diagenetic reactions, and reactions of impurities can influence the pH value.

By slight transport of water through the backfill material, the water composition is modified first of all through the solubility of the bentonite. Solution leads to a pH increase, e.g., the conversion of Na-smectite to kaolinite produces $H_LSiO_{L_2}$, Na⁺, and (OH)⁻.

Through use of literature values of montmorillonite solubility (161, 164) in model computations, the water composition may be ascertained on theoretical principles. However, difficulties arise in the selection of data.

Montmorillonite influences the water composition not only through its solubility but also through ion exchange. This influence was considered for a bentonite in model computations by Wanner (176).

A large number of experimental measurements of pH of waters in contact with clays under various conditions are discussed.

<u>Bentonite contains numerous organic and sulfide impurities</u>. Through their exidation with exygen in the initial phase of the final repository, the acidic reaction products CO_2 and SO_2 and/or SO_3 are formed. By heating up a natural clay with 1% pyrite and 0.2 to 1% organic impurities, acid condensates are formed (33, 36). In laboratory experiments, the pH value of the condensates amounted to 4.1 (50° C), 2.3 (100° C), and 1.4 (150° C). With "in situ" experiments, however, the pH value of the evolved condensed moisture in the same temperature region came out to from 5 to 6. The pH value in freshly exposed clay was determined to be 10.1 to 10.5. Comparison between laboratory and field experiments leads to the conclusion that, in large experiments, the clay mass acts as a buffer.

3.2 Water absorption and swelling of clay minerals

3.2.1 The swelling of montmorillonite

Smectite and vermiculite can absorb water between the layers and thereby swell. As A. Weiss (181) has already established in his classic work, the essential major influences for this process are:

-the surface density of the charge

-the charge and the solvation properties of the ions between layers

-the electrolyte concentration

Water sorption leads to the formation of colloidal dispersions in Na-smectite, while Ca-smectite has only a limited swelling capability.

4.2 Concepts and models

4.2.1 Cation exchange capacity

The cation exchange capacity of a solid, usually given in milliequivalents (meq) per 100 g, is a value which is affected by the measurement process. Usually, it is ascertained at pH7 with ammonium acetate (107). A comparison of different methods is found in Weiss (182). The cation exchange capacity is pH-dependent (16, 182). As an operationally fixed parameter, the cation exchange capacity says nothing about the sorption mechanism. This is to be borne in mind if this concept is applied to different types of materials, such as phyllosilicates, fine particle oxides, or <u>humic substances</u>.

Table 6 gives a compilation of cation exchange capacity of various silicates and some other substances.

(extract from) Table 6: Cation Exchange Capacity of Natural Substances (91)

Organic material	350 - 130 meq/100 g
Zeolites	300 - 100
Vermiculite	150 - 100
Montmorillonite	100 - 70
Tllite	40 - 10

4.2.4 The influence of ligands on cation adsorption

The influence of ligands on the sorption property of cations generally can not be predicted because, in a metal ion/ligand/sorbent system, a series of equilibria can be evolved, the position of which depends on the pH value, among others (cf. ref. 155, p. 132). If a ligand forms a stable dissolved complex without itself being adsorbed, sorption equilibria are shifted on the side of the dissolved metal. The uranium (VI) desorption through the formation of carbonate complexes at increased pH values is well known. Humic acids can function similarly.

The complex formed in solution can, however, also be adsorbed preferentially. This is, for example, the case for the adsorption of hydroxy complexes on smectites.

The ligand adsorbed on the surface of a solid material can bind cations in the form of binary surface complexes. In natural systems, a coadsorption of <u>humic acids</u> with metal ions might perhaps be expected. One such system was investigated by Tipping et al (167). At pH values below 6, copper is more strongly adsorbed on Goethite (alpha FeO·OH) in the presence of <u>humic acid</u>. At higher pH values, the concentration of dissolved <u>humic acid</u> increases. It is available only as dissolved <u>humic acid</u>, and, accordingly, less copper is adsorbed in the presence of <u>humic acid</u> (cf. Fig. 4.6 in ref. 155). Ho and Miller (71) report a similar finding in the hematite/<u>humic acid</u>/ uranium system.

4.3 Experimental results

4.3.2 Anions and weak acids

<u>Humic substances</u> are adsorbed on oxide surfaces. The adsorption on aluminum oxide of <u>humic substances</u> from Urner Lake (Switzerland) sediment is shown as a function of the pH value, the content of <u>dissolved organic</u> <u>carbon</u>, and the amount of solid alumina (34). On clay minerals, the binding of such substances is usually conceived as proceeding through hydrogen bonds or through multivalent cations (62, 63, 157) (Fig. 48). Such a <u>"numic acid/</u> clay complex" (63, p. 354) is predestined for the adsorption of further cations (167). Through the infiltration of <u>macromolecular organic substances</u> between layers, the cation exchange capacity of smectites is diminished ("clogging"). <u>Fulvic acids</u> appear to infiltrate in the space between layers of montmorillonite only at pH values below 4 (62), thus under conditions where, through partial dissolving of the montmorillonite, aluminum is set free and is placed in the space between layers.

8 SUMMARY OVERVIEW

Bentonites are clays with a high proportion of montmorillonite. They are selected as backfill material on account of their swelling ability and their sorption properties for cations. The properties being discussed depend closely on the layer structure of montmorillonite. The intensity of the layer charge and the type of cations between the layers can vary these properties over a wide region.

8.1 Clay/water systems

Bentonite influences the water composition through saturation of water by montmorillonite and through ion exchange. These reactions lead to a pH increase. Values of pH in the range of 8 to 10 are to be expected.

The pi value tends to be lowered by illite formation and also by the oxidation of <u>organic and sulfide impurities of bentonite</u> by oxygen. The acids formed thereby from the bentonite can be buffered as a result of the slow course of these reactions.