LONG TERM CORROSION OF GLASSES IN SALT BRINES

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Borosilicate glasses are supposed to be a suitable matrix for the fixation of calcined radioactive wastes. For the safety assessment of the disposal of these glasses in geological formations like carnallite or rock salt, their chemical durability in saturated salt brines has been investigated. Temperatures up to 200°C, pressures up to 130 bar, and corrosion times up to 5 years were applied. Special attention was given to the long term corrosion which is mainly characterized by the saturation of the corroding solution (leachate) with respect to silica.

Introduction

In the Federal Republic of Germany borosilicate glasses are proposed as waste form for the final disposal of high level waste (HLW) in geological salt formations. To check the safety of this waste form two different borosilicate glasses were corroded in salt brines typical of the respective geological formations. The aim of the investigations was to determine corrosion rates(dissolved mass of glass per surface area and corrosion time) and to understand the long term corrosion mechanisms, which is necessary to predict the corrosion behaviour of the waste form for longer periods (several 100 years).

Many results are published about the corrosion of glasses in aqueous solutions containing only minute amounts of dissolved material. High concentrated salt brines are rather unusual corrosion media. Nevertheless, results of "short term" corrosion tests (corrosion time t $\leq$ 1 year) have already been published by several authors. An evaluation [1] of published results concerning the corrosion of HLW glasses in different media (deionized water, silicious groundwaters, salt brines) showed that in most cases - independant of the applied corrosion medium - the following mechanisms were observed:

network dissolution,

formation of reaction product layers on top of the surface of the undissolved glass, and

the alteration of a comparably thin surface zone of the undissolved glass by ion exchange.

The mass loss of the glass is almost totally due to network dissolution. The reaction product layer may partly be generated by the transformation of a highly depleted and hydrolyzed network, partly by the re-precipitation of initially dissolved glass constituents. The layer determines the chemistry of the leachate as precipitate, but has only a minor effect on the corrosion rates. This was demonstrated (glass and corrosion conditions identical to those of the long term corrosion tests reported here) by removing the layer and subsequent corrosion of the glass in the unchanged leachate [2]. The surface of the glass is altered by ion exchange to a depth of < 0.5 μm [3].

Only a few results have been published of tests running for longer periods. Strachan et al. [4] reported tests with a duration of up to two years at 40 and 90°C. They found that the corrosion rates for a borosilicate glass with 38.7 SiO_2, 9.8 B_2O_3, and 14.8 Na_2O (wt.-%) in salt brines are lower than those in deionized water or groundwater systems. After about 1 or 1.5 years the corrosions process is slowed down.

Some studies focused on corrosion mechanisms. Grambow [5] interpretated the corrosion process as network dissolution at the interface reaction product layer - glass. The corrosion rates are determined by the activity of H_4SiO_4 in solution and by the rate constants of the two competing reactions hydrolysis of Si-O-metal or Si-O-Si bonds (1) and the condensation of silanol groups (2).

The effect of the silica saturation (in this paper: the saturation of the leachate with respect to a silica containing species) on the corrosion process is discussed by several authors [e. g. 2, 6 - 9]. Pederson et al. [6] showed for corrosion tests in deionized water with varying S/V ratios (S/V: surface area of glass / leachant volume), that the corrosion process can be accelerated by applying high S/V ratios. They proposed (within some limitations) short term tests at high S/V ratios to simulate long term corrosion conditions.

Van Iseghem and Grambow [7] investigated the corrosion of two glasses in destilled water. They showed for a borosilicate glass with a high alumina content (18.1 wt.-%), that the corrosion proceeds after silica saturation. Concerning the HLW glass SM 58 (subject of this paper), they could not state whether the same is valid or not.

Freude et al. [8] corroded a barium alumosilicate glass up to 120 d in a saturated NaCl brine (S/V ratios: 10-100 m^{-1}). They used a linear time law to describe the corrosion progress after

reaching silica saturation. Lutze et al. [9] approved for the borosilicate glass SON 68 (corroding in a salt brine at 110, 150, and 190°C; variation of S/V ratio) that the glass dissolution continues after silica saturation at a low rate supposed to depend linearly on S/V·t. Their results indicated that transport processes may control the corrosion rate in the long term.

To summarize, most authors expect that the corrosion of HLW glasses in aqueous solutions as well as in salt brines starts with a corrosion rate depending linearly on time. After a certain time this rate is expected to slow down to a final rate again linearly depending on time which is typical of the long term corrosion range characterized by silica saturation. This is concluded from the results of corrosion tests simulating the long term corrosion conditions by applying high S/V ratios, whereas similar results of "real" long term (t > 2 years) tests are lacking.

The invesigations presented here started seven years ago. The results of the "short term" corrosion tests have already been published [3]. The results of the long term tests (up to 5 years) are presented here.

Experiments

The glasses have been corroded in steel autoclaves with teflon containers inside without renewing the leachates during the tests. The leachant volume was 90 cm^3, the size of the glass chips 0.9 x 1.2 x 0.2 cm^3. The ratio S/V of the glass surface area to solution volume was 3.3 m^{-1}. Corrosion temperatures between 80 and 200°C, pressures up to 130 bar (the pressure has only a slight influence on the corrosion rates; this was proved by comparison with identical corrosion tests at equilibrium pressure), and corrosion times up to 5 years were applied.

The salt brine contained 26.8 $MgCl_2$, 4.7 KCl, 1.5 NaCl, and 1.4 $MgSO_4$ (in wt.-%; rest water). The composition of the investigated HLW glass SM 58 is listed in Table 1.

Table 1. Composition of the HLW glass SM 58 in wt.-%

component	SiO_2	B_2O_3	Al_2O_3	Li_2O	Na_2O	MgO	rest
SM 58	56.8	12.3	2.1	3.7	8.0	2.1	15.0

The corrosion tests were evaluated by balancing the glass chips and chemical analysis of 'the leachate and the layer of reaction products on top of the glass. The layer consisted of precipitates from the solution or strongly altered glass and could be removed easily. The mass loss of the reacted glass was calculated from the boron content of the leachate, which is possible if the mass loss is almost totally due to the dissolution of the glass network, or by balancing. By both methods comparable results were obtained.

The results for t > 100 d are presented in Fig. 1a-b. For comparison, the data of the short term tests at 160 and 200°C are presented in Fig. 2. Data points at t ≥ 730 d represent an average of 5 different samples. For t ≤ 365 d, only three samples were analyzed. The standard deviation for the long term data points (3 and 5 years) was better than 4 % (160 and 200°C) or 8 % (120 °C). At 80°C, the standard deviation was ≤ 80 %, which is rather high.
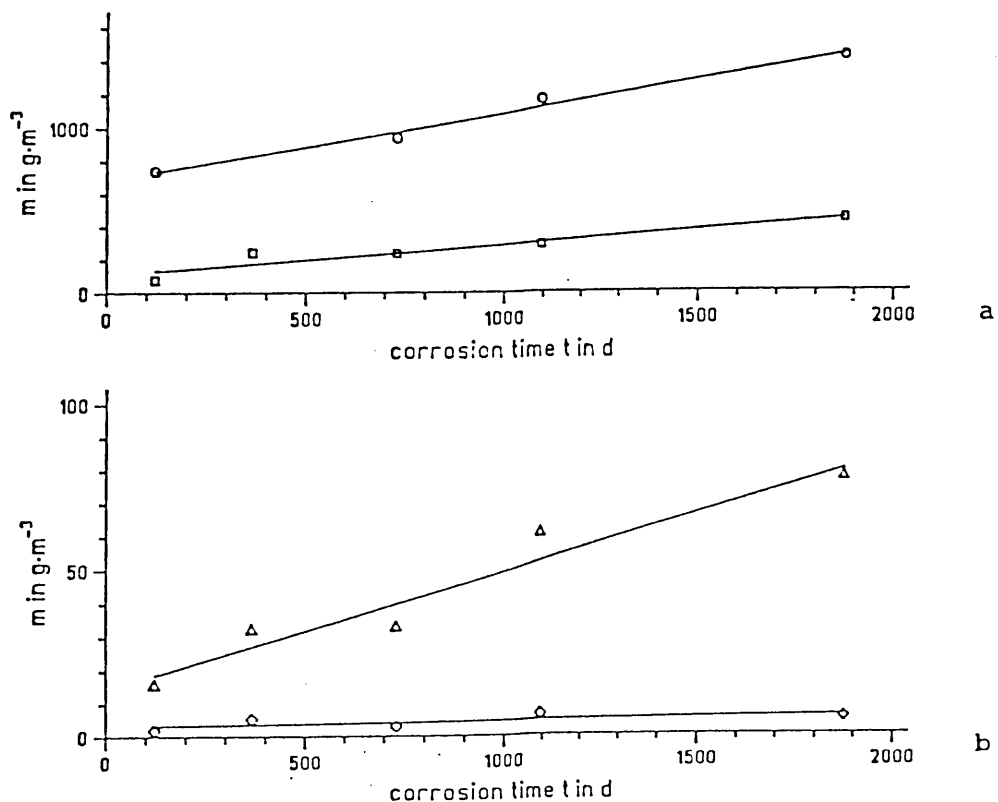

Fig. 1a-b. Mass of reacted glass per leachant volume m as a function of the corrosion time t; corrosion of HLW glass SM 58 in a concentrated salt brine (composition given above); pressure: 130 bar; corrosion temperature:
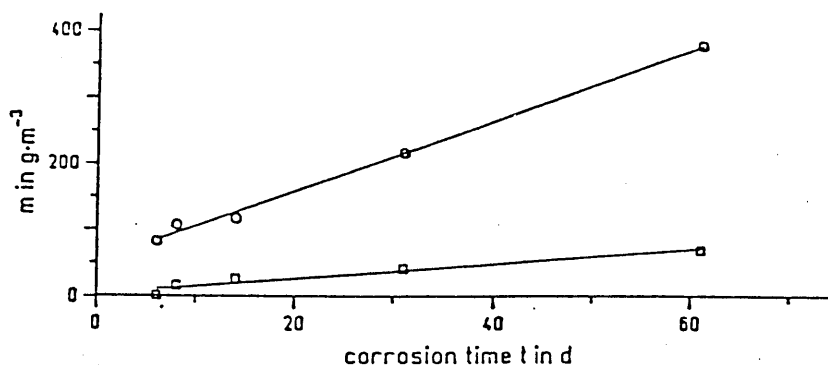◇ : 80°C; △ : 120°C; □ : 160°C; o : 200°C;

Fig 2. Same as Fig 1a-b, but t < 100 d ("short term" range);
□ : 160°C; o : 200°C

The mass of reacted glass increases with corrosion time for all test temperatures in the observed time range. An evaluation of the data according to a linear time law yielded the corrosion rates listed in Table 2. The values of the ordinate intercepts are always > 0. This is due to the drastic decrease of the corrosion rate after about 100 d. For comparison the corrosion rates determined for t < 100 d are also listed in Table 2.

Table 2. Long and short term corrosion rates for the HLW glass SM 58 corroding in a concentrated salt brine

	corrosion rates in $g \cdot m^{-2} \cdot d^{-1}$	
	t < 100 d	t > 100 d
80°C	0.10	0.005
120°C	0.62	0.115
160°C	3.6	0.59
200°C	18.1	1.31

Discussion

According to Lutze et al. [9] the silica saturation values for applied salt brine are 57 $g \cdot m^{-3}$ (110°C), 121 $g \cdot m^{-3}$ (150°C), and 170°C (190°C). Although they investigated a slightly different borosilicate glass (45.5 SiO_2, 14.0 B_2O_3, and 9.9 Na_2O; in wt.-%) and used other corrosion temperatures, one can conclude that in the tests reported here the state of silica saturation was reached for the 120°C (at least after five years), the 160°C (after 1 year), and the 200°C (after 120 d) tests. The same can-

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not be stated for the corrosion at 80°C (due to lacking data for silica saturation and to the poor precision of the reported measurements. The chemical analysis of the solution showed, that at 160 and 200°C silica is partly present as precipitate. As the solutions were cooled down to room temperature for analyzing, this observation does not allow to state the presence of a precipitate at corrosion temperature. Nevertheless, in all cases a drastic decrease of the corrosion rate was observed after a corrosion time t > 100 d, leading to the conclusion, that the long term corrosion range was reached. Therefore the presented results ensure the finding of simulated long term test, that the corrosion process proceeds after reaching silica saturation. But even the data of the 5 year tests do not allow to decide, whether the time law for the long term corrosion is linear or not. For safety assessments it is advisable to use a linear time law.

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