

ENCAPSULATION OF GRANULAR ION-EXCHANGE RESINS IN SOLID FORM WITH ALKALI-ACTIVATED BLAST- FURNACE SLAG



A. Ipatti
Ms.Sc.(Eng.), Research Engineer
Imatran Voima Oy,
Research and Development Division,
Rajatorpantie 8, SF-01600 Vantaa, FINLAND

Abstract

The liquid low- and intermediate-level wastes from the Loviisa nuclear power plant will be solidified before the final disposal by mixing them with a suitable cementitious material. Satisfactory waste product properties in encapsulation of granular ion-exchange resins in solid form have so far been achieved by using Portland or blast-furnace slag cements as a binder. The scope of the present study was to investigate whether the technical properties of the waste product and the efficiency of the solidification could be improved by replacing the cement by alkali-activated blast-furnace slag.

Key words: alkali-activation, blast-furnace slag, cementation, encapsulation, ion-exchange resins, reactor wastes, solidification.

1. INTRODUCTION

The primary circuit water of a nuclear power plant is continuously circulated through the purification system based on ionexchangers. Since a part of the impurities in the water will become radioactive in the reactor, the ion-exchange resins used as filter masses are classified as radioactive waste.

For the time being, the spent ion-exchange resins produced during the operation of the Loviisa NPP are pumped into storage facility located within the plant area. However, this kind of storing is not possible indefinitely. It is in connection with the decommissioning of the nuclear power plant, at the latest, that the resins shall be conditioned to be fit for disposal and transported to a repository outside the human environment. Before the final disposal, ion-exchange resins are solidified by mixing them with a suitable solidification agent. At Loviisa cement has been chosen to be used as solidification material.

Imatran Voima Oy (IVO) has been conducting research on the cement solidification of ion-exchange resins and other liquid reactor wastes since the end of the 70s. The objectives of the studies

have been to find suitable mix proportions for the solidification process and to determine the properties of the waste product required by the safety analysis of the final disposal /1-4/.

One of the problems with the solidification of granular boric acid containing ion-exchange resins is the set retarding effect of the boric acid (H_3BO_3) present in the resins. Another problem is the interaction between the cement and the water in the resin. During mixing and then setting, some of the water trapped in the structure of resin grains is released due to the heat generated in cement hydration. While releasing water the grains shrink and come loose from the surrounding matrix. Later, when the waste product comes in contact with water, the resin grains will regain water thus swelling and possibly cracking the product.

Satisfactory waste product properties in solidification of this kind of resin have so far been achieved by using Portland or blast-furnace slag cements as a binder. In order to saturate the free ion-exchange sites of the resin beads and to eliminate the neutralization of basic cement matrix, $Ca(OH)_2$ or NaOH has been used as an additive in waste product mixtures.

The scope of the present research was to investigate whether the technical properties of the waste product and the efficiency of the solidification could be improved by replacing the cement by cheaper blast-furnace slag, the latent hydraulic properties of which are activated with a suitable inorganic material. The activators used, each with various dosages, included NaOH, $Ca(OH)_2$, Na_2SiO_3 and Na_2CO_3 .

If ground vitreous slag is mixed with water, a small amount of calcium cations is released in the solution while an acid surface layer is formed on the slag grains. The function of the activator is to break down the layer and in this way to facilitate the formation of hydrates and the penetration of water. The hydraulic activation of latent slag is based on the influence of either hydroxide or sulphate ions. Alkali metal silicates, hydroxides and salts of weak acids have been mentioned as suitable activators for basic and neutral slags /5-7/. The suitability of an activator depends on chemical composition, alkalinity and glass content of the slag.

In solidification of ion-exchange resins, alkaline activators are not only activating the hydration of slag but they are also neutralizing the acid resin/water mixture and saturating the free ion-exchange sites of the resin grains. Therefore, it is well founded to suppose that the required activator doses will be higher than normally used in concrete technology.

2. EXPERIMENTAL DETAILS

2.1 Materials

Water saturated resin mixture having the following properties was used in the tests; pH 3.3, density 1.13 kg/m^3 , water content 69.6% and boric acid content 53 g/l. The resin mixture was a compound of granular Amberlite 200C cation resin (in H^+ form) and Amberlite IRA 900C anion resin (in OH^- form) in the volumetric proportion of 1:1. A photomicrograph of dried anion resin grains is presented in Figure 1.

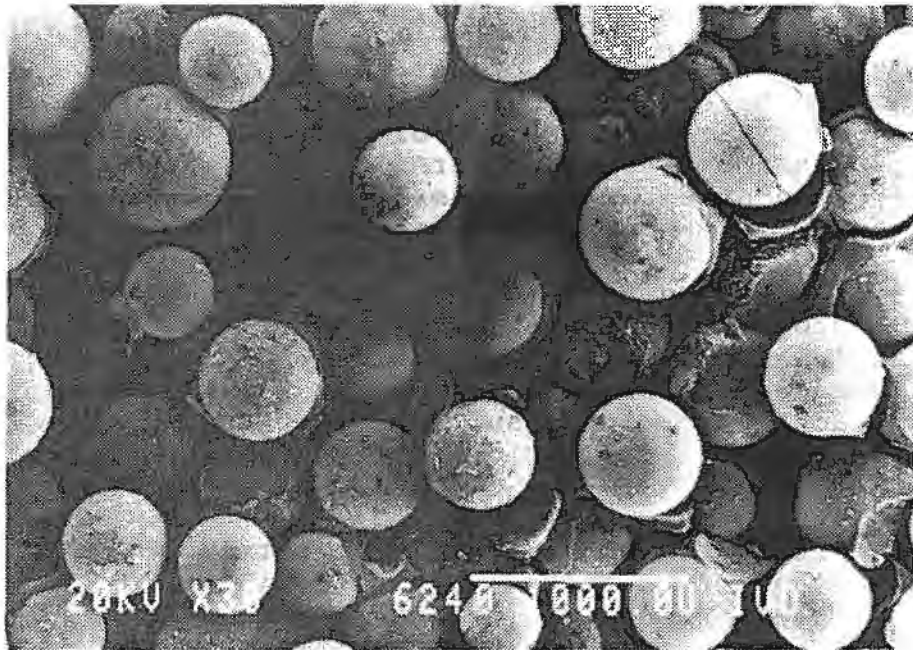


Figure 1. Photomicrograph (SEM) of the granular resins used in the study. Between the resin grains there are remnants of graphite glue used for pasting of the grains on the base.

The blast-furnace slag used was alkaline granulated slag, the fineness of which was $700 \text{ m}^2/\text{kg}$. In the reference waste products the binder was slow hardening blast-furnace slag cement (M40/91 LH SR) and normal hardening Portland composite cement (Y40/28). The slag content of the blast-furnace slag cement was about 72%. The chemical compositions and physical properties of the cements and blast-furnace slag are presented in Table 1.

On the basis of the literature [5,6,7], the following chemicals of a technical grade were chosen for alkali activation of the blast-furnace slag: calcium hydroxide ($\text{Ca}(\text{OH})_2$, powder), sodium hydroxide (NaOH , 50% solution), sodium metasilicate (Na_2SiO_3 , 35-45% solution) and sodium carbonate (Na_2CO_3 , powder).

The extra water used in the solidification was tap water. The storage water of the test specimens was groundwater taken from the planned disposal site; the chloride, sulphate and magnesium contents of this water were 5540, 692 and 282 mg/l.

Table 1. Properties of the cements and blast-furnace slag used in the research.

	M40/91 LHSR	P40/28	Slag	
Physical properties:				
Vicat setting time				
Initial	h:min	3:20	2:00	-
Final	h:min	4:30	3:00	-
Density	kg/m ³	2990	2980	2880
Blaine fineness	m ² /kg	480	360	720
Compressive strength				
2d	MN/m ²	-	19	-
7d	MN/m ²	20	33	-
28d	MN/m ²	45	48	-
91d	MN/m ²	57	62	-
Chemical analyses:				
CaO	%	58.3	55.3	38.7
SiO ₂	%	20.9	24.2	34.3
Fe ₂ O ₃	%	4.0	2.4	1.3
Al ₂ O ₃	%	2.8	2.6	8.4
MgO	%	2.2	1.6	10.2
SO ₃	%	1.5	0	2.8
Na ₂ O+K ₂ O	%	1.4	1.4	-
LOI	%	<0.1	5.1	<0.1

2.2 Test programme

The test programme consists of successive pretests and solidification tests.

The objective of the pretests is to chart rapidly (in two weeks), with small testpiece and waste amounts, the mix proportions suitable for cement solidification. In the pretests, the solidification products were analyzed for their spread value (DIN flow table) and setting time (Vicat).

On the basis of the pretest results, compositions for more extensive solidification tests were chosen; the objective of these tests was to determine basic properties of fresh and hardened solidification products. The fresh solidification products were tested for their spread value, density, air content, setting time and bleeding. The hardened solidification products were analyzed for their compressive strengths and deformations. The test specimens of 40 x 40 x 160 mm were stored three months both in sealed conditions and in groundwater.

In all test mixtures, the mass proportion of binder and water saturated resin was 2:1. The test mixtures were prepared with a universal mixer in the following order of dosage: water saturated resin, additive, binder and extra water, the total mixing period being 5-6 min. The amount of extra water for the test mixtures was chosen so that the spread value of the waste product in the DIN flow table test was 180-230 mm.

3. RESULTS AND DISCUSSION

The pretests were performed with the 14 test mixtures listed in Table 2. Pretest mixtures AE1 and AE2 are reference mixtures chosen on the basis of previous tests.

Table 2. Mix proportions (in weight parts), setting times (h:min) and spread values (mm) of the pretest mixtures.

MIX No.	MIX PROPORTIONS				SETTING TIME		SPREAD VALUE		
	Resin	Binder	Activator	Water	Initial	Final			
AE1	1	BFL	2	Ca(OH) ₂	0.18	0.53	1:10	3:00	185
AE2	1	P.Co	2	NaOH	0.12	0.31	1:30	2:15	205
AE3	1	Slag	2	Ca(OH) ₂	0.09	0.67	>48:00	>48:00	182
AE4	1	Slag	2	Ca(OH) ₂	0.18	0.77	42:00	>48:00	180
AE5	1	Slag	2	Ca(OH) ₂	0.27	0.83	27:30	>48:00	180
AE6	1	Slag	2	NaOH	0.12	0.48	>48:00	>48:00	182
AE7	1	Slag	2	NaOH	0.15	0.50	15:30	18:15	189
AE8	1	Slag	2	NaOH	0.18	0.49	9:30	13:30	195
AE9	1	Slag	2	Na ₂ SiO ₃	0.12	1.10	>48:00	>48:00	170
AE10	1	Slag	2	Na ₂ SiO ₃	0.18	1.53	>48:00	>48:00	190
AE11	1	Slag	2	Na ₂ SiO ₃	0.24	1.70	>48:00	>48:00	182
AE12	1	Slag	2	Na ₂ CO ₃	0.06	0.55	>48:00	>48:00	180
AE13	1	Slag	2	Na ₂ CO ₃	0.09	0.48	0:45	5:00	225
AE14	1	Slag	2	Na ₂ CO ₃	0.12	0.49	>48:00	>48:00	230

The pretest results indicate that Na₂SiO₃ and Na₂CO₃ do not properly activate the hydration of the slag in the acid resin/water environment. On the other hand, satisfactory activation was achieved with rather high doses of Ca(OH)₂ and with moderate doses of NaOH.

On the basis of pretests, only four test mixtures were chosen for the solidification test. The compositions of these mixtures are listed in Table 3 and their properties in Table 4 and in Figures 2 - 3.

Mixtures A1, A2 and A3 are as such similar to pretest mixtures AE1, AE2 and AE7. Mixture A4 corresponds to pretest mixture AE5, however, the calcium hydroxide dose has been increased to 0.30 weight parts.

Table 3. Proportions and efficiency factors for waste product mixtures.

MIXTURE No.	A1	A2	A3	A4
Mix proportions (kg/m³):				
Water saturated resin	450	516	455	398
Cement or slag	900	1032	910	795
NaOH or Ca(OH) ₂	81	62	68	119
Extra water	239	160	227	298
Total	1670	1770	1660	1610
Efficiency factors:				
Volume increase factor	2.51	2.19	2.48	2.84
Mass increase factor	3.71	3.43	3.65	4.04
Water-binder-ratio	0.61	0.56	0.67	0.72
Content of solid waste in waste product (W.-%)	8.2	8.9	8.3	7.5

Volume increase factors of the test mixtures A1 - A4 varied between 2.19 and 2.84, i.e. by solidifying 1 m³ of liquid waste we get 2.19 - 2.84 m³ of waste product to be disposed of. The smallest volume increase factor was in reference mixture A2 and the largest one in mixture A4. Binder amounts of the test mixtures were quite large, about 800-1000 kg/m³, which may result in considerable hydration heat generation during hardening of the solidification product.

Table 4. Properties of the fresh waste product mixtures.

MIX No.	CONSISTENCY (mm)	AIR (l/m ³)	BLEEDING			SETTING TIME		DENSITY (kg/m ³)
			3h	1d	7d	Initial	Final	
A1	185	26	0.0	0.0	0.0	1:10	3:00	1670
A2	205	13	0.0	0.0	0.0	1:30	2:15	1770
A3	190	16	0.4	0.7	0.0	15:30	18:15	1660
A4	182	28	0.2	0.6	0.2	27:30	45:00	1610

Target consistency used for the test mixtures was the spread value of 180-230 mm in DIN flow table test. Spread values of all test mixtures were within the specified range.

The allowed upper limit of the final setting time for the waste product has been considered to be 24h. Of the compared test mixtures, mixture A4 did not fulfill this requirement.

A further requirement is that no free (uncombined) water is allowed on the surface of the waste product within 24h after preparation of the mixture. Mixtures A1 and A2 fulfilled this requirement, but in mixtures A3 and A4 the bleeding was heavy.

There are no specific requirements for density and air content of the waste product. The measured values of the mixtures varied between 1610 and 1770 kg/m³ and between 13 and 28 l/m³.

The required compressive strength of the solidification product at the age of 28d is 5 MN/m². In addition, it is required that the compressive strength value of 91d is not lower than that of 28d. Sealed storage of test specimens represents the situation inside the disposal container, where there is no moisture exchange between the waste product and the environment. Water storage corresponds to the situation where the disposal container is cracked and groundwater is in contact with the solidification product.

All compared test mixtures fulfilled the compressive strength requirements, see Figure 2. The 28d strengths of the test mixtures varied between 9 and 19 MN/m² and the 91d strengths between 15 and 25 MN/m². In the initial stage, the strength development was quickest in mixtures A2 and A3 containing NaOH. The groundwater storage does not seem to have any essential significance on strength development.

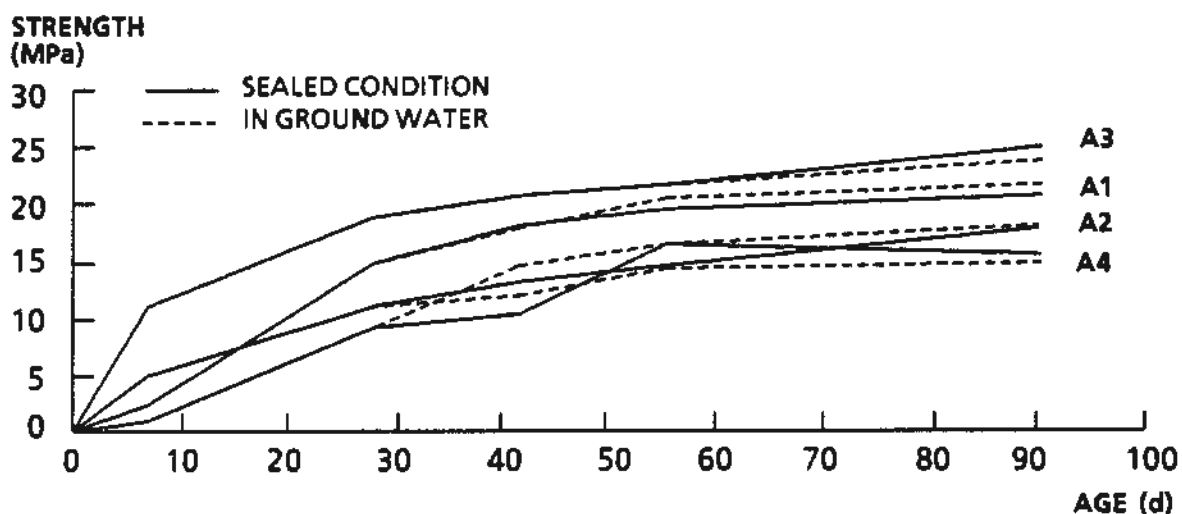


Figure 2. Compressive strength developments.

So far there are no exact requirements for deformations of solidification products. Expansion of the solidification product results from hydration heat generation of the binder and from moisture expansion of the resin grains when they absorb moisture from the surrounding cement matrix. Correspondingly, shrinkage of a product results either from moisture evaporation or from the fact that the volume of the reaction products formed in hydration is smaller than the total volume of the originally reacting materials.

In the sealed condition, test mixtures A1, A2 and A4 have expanded in such a way that their deformations at the age of 91d were 1.4, 2.6 and 0.3 mm/m, respectively (Figure 3). Instead, test mixture A3 has shrunk steadily right from the beginning so that its deformation at the age of 91d was about -0.4 mm/m. In water storage, all test mixtures have expanded so that the moisture expansion values during the period from 28d to 91d were: 0.369 mm/m for mixture A1, 0.919 mm/m for mixture A2, 0.335 mm/m for mixture A3 and 0.451 mm/m for mixture A4.

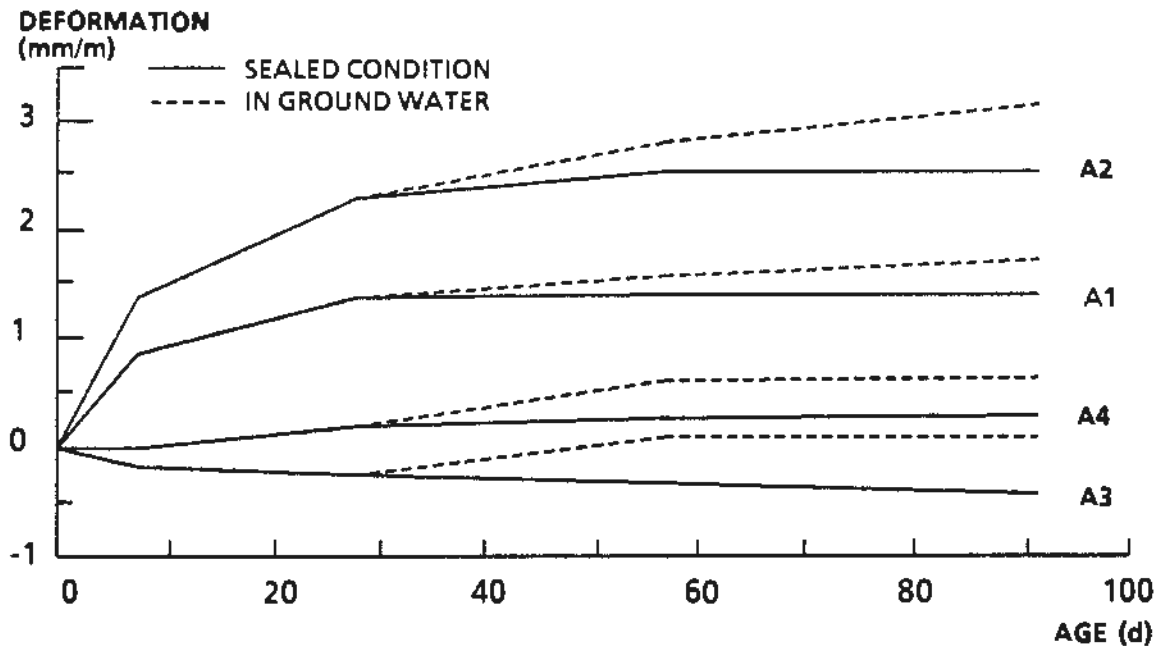


Figure 3. Linear volume changes in sealed conditions and in groundwater storage.

4. CONCLUSIONS

On the basis of the test results, the following conclusions can be made :

- a. In cement solidification of ion-exchange resins, alkaline additives are used to control pH value of the resin-water mixture and to saturate the free ion-exchange sites of resin grains. If blast-furnace slag is the only binder, alkaline additives are also needed for activation of hydration reactions of the slag.
- b. The use of alkaline activators in the liquid state is more advantageous in view of solidification efficiency than the use of powdery activators. This is resulted from relatively high doses of powdery activators, which increases the extra water needed for the solidification mixture.
- c. Na_2SiO_3 and Na_2CO_3 do not properly activate the hydration of the slag in the acid resin/water environment. On the other hand, satisfactory activation was achieved with rather high doses of $\text{Ca}(\text{OH})_2$ and with moderate doses of NaOH .
- d. The technical properties of the waste product and the solidification efficiency were not improved sufficiently to justify the replacement of Portland or blast-furnace slag cements with alkali-activated slag.

5. REFERENCES

1. Ipatti, A., Solidification of ion-exchange resins with alkali-activated blast-furnace slag. E-MRS 1991 Fall Meeting, Strasbourg, France, 4-8 November 1991. Symposium D: Chemistry of Cements for Nuclear Applications. D.II.2, 6p.
2. Ipatti, A., Cement solidification of spent ion-exchange resins - Intermediate results of a half-scale experiment. Nuclear Waste Commission of Finnish Power Companies. Report YJT-90-19, 1990. 47p.
3. Aalto, H., Ipatti, A., Leach test of spent ion-exchange resins solidified in concrete. E-MRS 1991 Fall Meeting, Strasbourg, France, 4-8 November 1991. Symposium D: Chemistry of Cements for Nuclear Applications. D.IV.2, 6p.
4. Ipatti, A., Härkönen, H., Half-scale cementation of spent ion-exchange resins at the Loviisa nuclear power plant. BNES conference on Radioactive Waste Management, May 2-5, 1989, Brighton. Proceedings, V. 1, pp. 67-70.
5. Häkkinen, T., Properties of alkali-activated slag concrete. Technical Research Centre of Finland, Research Notes 540. Espoo 1986, 62p.
6. Metso, J., Kajanus, E., Activation of blast furnace slag by some inorganic materials. In: Fly ash, silica fume, slag & other mineral byproducts in concrete. Detroit, ACI-publication SP-79, V.II, pp.1059 - 1073.
7. Talling, B., Brandstetter, J., Present state and future of alkali-activated slag concretes. In: Fly ash, silica fume, slag and natural pozzolans in concrete. Detroit, ACI-publication SP-114, V.II, pp. 1519 - 1546.