Geopolymerisation of gasified ion-exchange resins, mechanical properties and short-term leaching studies

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Abstract. A combination of gasification of low and intermediate level radioactive waste (LILW) and conditioning of the resulting product within a geopolymer matrix is a potential alternative for vitrification technologies as an immobilisation method. Geopolymer matrices have demonstrated good retention capability for radionuclides in many studies and the technology has been implemented at an industrial scale in Slovakia and Czech Republic. However, the practical waste loading has been limited by the mechanical properties of the encapsulated matrix. Even a small amount of ion exchange resin (IXR) decreases the strength of the matrix and cohesion of the matrix is lost when the fraction of resin exceeds 15-20%. In this study, the potential to combine gasification as thermal treatment and various inorganic binders as encapsulation matrices was evaluated. After gasification, the mechanical properties were not similarly sensitive to the encapsulation of IXR. Gasification enabled substantially higher loading of IXR into the sample. Also, gasification of the IXR decreased matrix apparent Caesium diffusion. Very low apparent diffusion coefficients of Cs were calculated when gasified resin was encapsulated in metakaolin matrix. Theoretically, the amount of Cs within the same volume of encapsulated material could be increased by 800 times following gasification and encapsulation within an alkali-activated metakaolin (MK) binder.

1. Introduction

Nuclear wastes are traditionally classified into three categories depending on the material's radioactivity. High level radioactive wastes (HLW) consists of spent nuclear fuel and other high activity products. In Finland, low and intermediate level radioactive wastes (LILW) are items and materials that are contaminated or activated by the operation of a nuclear power plant. LILW contains only 1% of the total radioactive inventory produced by the nuclear industry. However, it represents more than 95% of the total volume of radioactive waste. Partly, due to this high volume, issues related to final disposal of HLW and LILW are very different.

HLW must be isolated from the biosphere for hundred thousand years or even longer. For LILW, the timespan is only from hundreds to thousand years. Relatively small volume of HLW enables use of expensive encapsulation materials (e.g. copper canisters) and deep underground disposal (400-500 meters below ground surface) [1]. With LILW, encapsulation with a binder is usually sufficient and the repositories can be at shallower depth than the HLW repositories.

Binders for LILW encapsulation should stabilize wastes and retard dissolution of radionuclides. Binders from the construction industry are often used due to high availability and low price (e.g. Portland cement and bitumen). However, both have their weaknesses. Bitumen is a combustible material and

potential fire could cause release of radionuclides into the environment. Cementitious materials are not combustible but they are vulnerable to various chemical alterations. Small amounts of dissolving organics can prevent hardening process of a cement and even some elements have similar effect (e.g. boron). Hardened Portland cement has also poor adhesion to solid organic materials, which decreases the strength of the cementitious matrix in encapsulation.

Because of the above described reasons, the amount of encapsulated ion-exchange resins (IXR) that can be incorporated in the cementitious matrix is only 10-15% in industrial scale encapsulation. With larger amounts, cohesion of the encapsulation matrix is lost. As the IXR forms a major part of the Finnish ILW inventory, most of the repository space is occupied by supplementary materials, taking space from the actual radioactive waste.

Thermal treatments of IXR are able to reduce the volume of the radioactive waste significantly. Due to removal of organic content in IXR, the volume of the thermally treated material reduces to 1-5% of the original volume [2]. However, remaining radioactive ashes must be encapsulated. Vitrification, encapsulation simultaneously into a glass phase has already been studied.[3]

Another option is to perform thermal treatment and encapsulation sequentially. Gasification is a thermal treatment that can remove organic matter from IXR without release of radionuclide quantities. Binders that are traditionally used for encapsulation are potential option to bind the gasified resins. However, many studies present that alternative inorganic binders have higher radionuclide bounding capacity. Specially, metakaolin (MK) has been used in industrial scale encapsulation in Czech Republic and Slovakia [4]. Increased binding capacity of the encapsulation matrix might become a necessary in gasified resins, as the radionuclide content in the encapsulation increases significantly.

In this study, the potential to combine gasification as thermal treatment and various inorganic binders as encapsulation matrices was tested. Evaluation was performed to Ordinary Portland Cement (OPC), alkali-activated blast furnace slag (BFS) and alkali-activated metakaolin (MK). Results were compared to traditional pristine resin/OPC encapsulation and existing guidelines. Evaluation was performed using inactive cesium tracer as cesium (^{137}Cs, ^{134}Cs) is the main source of radioactivity in IXR within the first 200-300 years.

2. Materials and Methods

Organic IXR was doped with cesium tracer (^{133}Cs). After the doping, the IXR was gasified at 850 °C, steady-state measuring period being 5 hours. Cesium content of the pristine resin was 3.8 mg/kg, and gasified resins Cs content was 70.7 mg/kg. Cs content were measured by dissolving samples and determining the Cs concentration with sector field Inductively Coupled Plasma mass-spectrometer (SF-ICP-MS) (Element 2™ ThermoScientific).

Prior to analysis of cesium, approximately 50 m of resin sample was weighed and solution was added into Teflon vials. A mixture of concentrated 4 ml HNO_3 (suprapure, s.p) and 0.5 ml H_2O_2 was used for resin samples and 2 ml HNO_3 (s.p), 1.5 ml HF and 2 ml $HClO_4$ for ash samples. The microwave assisted digestion was run with SRC (single reaction chamber) Ultrawave system by Milestone. Chamber was pressurized to 40 bar and temperature was ramped up in steps 1) 10 min to 60°C, 2) 10 min to 200°C, 3) 5 min to 230°C, and 4) finally kept 10 min at 230°C before cooling down.

After gasification, ashes were homogenized and mixed with studied binder. Ash dosing was calculated as a pristine resin and is presented in Table 1. Studied binders were Ordinary Portland cement CEMI (Annläggninscement from Degerhamn, Cementa Ab), blast furnace slag (Masuunikuonajauhe KJ100, Finnsementti Oy) and metakaolin (Metastar from BASF). Alkaline activators and water was premixed. Potassium hydroxide (Sigma Aldrich, reagent grade) and sodium silicate solution (Zeopol 33 from Huber Engineered Materials) were used as activators. Solution was left to cool down to room temperature prior to sample batching. The resulting solution was combined with solid materials and the mix was agitated for three minutes. Samples were cast into moulds and BFS and MK samples were cured for 24 hours in 80°C at relative humidity 100%. OPC samples were cured in autogeneous conditions at room temperature for 24 hours. Samples were demoulded and cured in autogeneous

conditions in room temperature for an additional 6 days. Mix designs of the studied samples are presented in Table 1.

Table 1. Mix designs of the studied samples in measurement of the leachability of solidified low-level radioactive wastes by a short-term test procedure.

Binder system		Dosing /%	Binder /g	Pristine resin /g	Gasified resin /g	Water /g	Sodium silicate[a] /g	Potassium hydroxide /g
OPC	doped resin	13	1000	200	-	400	-	-
OPC	gasified resin	10	1000	-	8.5	400	-	-
BFS	gasified resin	10	1000	-	8.2	105	178.5	119
MK	gasified resin	10	1000	-	14.1	-	1177	202
OPC	gasified resin	20	1000	-	18.7	400	-	-
BFS	gasified resin	20	1000	-	18.8	105	178.5	119
MK	gasified resin	20	1000	-	31.6	-	1177	202
OPC	gasified resin	50	1000	-	74.5	400	-	-
BFS	gasified resin	50	1000	-	74.6	105	178.5	119
MK	gasified resin	50	1000	-	126.6	-	1177	202

[a] Solid content of sodium silicate was 37%.

Leachability of the Cs tracer from the samples was studied according to American Nuclear Society standard: *Measurement of the leachability of solidified low-level radioactive wastes by a short-term test procedure* [5]. In the tests, samples with cylinder geometry were exposed to ion-exchanged water for a certain time periods. Water content was tenfold respect to the surface area of the sample. The concentration of leached tracer was measured and based on the results, Cs apparent diffusion coefficient was calculated. Cs apparent diffusion coefficients were calculated according to Equation 1. Detailed description of the method is available elsewhere.[4] The amount of leached Cs tracer was determined using SF-ICP-MS.

$$D = \pi \left[\frac{a_n/A_0}{(\Delta t)_n}\right]^2 \left[\frac{V}{S}\right]^2 \left[\frac{1}{2}\left(t_n^{1/2} + t_{n-1}^{1/2}\right)\right]^2 \tag{1}$$

In Equation 1, D is the apparent diffusion coefficient (cm^2/s), a_n is the quantity of a tracer released from the specimen (mol), A_0 is the total quantity of a tracer (mol), t is the time (s), Δt in the leaching interval (s), V is the volume of the specimen (cm^3) and S is the geometric surface area of the specimen as calculated from measured dimensions (cm^2).

The influence of the pristine IXR and gasified resin to mechanical properties of OPC matrix was studied. Mix designs reported in Table 2 were cast and the compression strength of the samples were determined at the age of 7 days according to [6].

Table 2. Mix designs of studied samples in compression strength studies.

Binder system		Resin/binder content /%	Binder /g	Pristine resin /g	Gasified resin /g	Water /g
OPC	pristine resin	1	1000	14.1	-	400
OPC	pristine resin	5	1000	73.7	-	400
OPC	pristine resin	10	1000	155.6	-	400
OPC	pristine resin	15	1000	247.1	-	400
OPC	gasified resin	1	1000	-	14.1	400
OPC	gasified resin	5	1000	-	73.7	400
OPC	gasified resin	10	1000	-	155.6	400
OPC	gasified resin	15	1000	-	247.1	400

3. Results

Cesium concentrations from short-term leaching test procedure are presented in Table 3. Dosing of resin is presented as pristine resin, calculated from cesium content of pristine resin and gasified resin. Gasification of the IXR changed the resin's behaviour in the leaching test. The amount of leached cesium decreased due to gasification treatment of the resin. Concentration of the leached cesium was approximately ¼ in OPC/gasified resin samples compared to OPC/pristine resin samples. Even greater difference was observed when the binder was changed to BFS or MK. With BFS/ gasified resin samples, the concentration of leached cesium was approximately 1/10 compared to OPC/pristine resin samples. It should be noted that during sequential leaching, leached cesium concentrations decreased in OPC-based samples whereas concentrations in BFS-based samples tend to increase. Cesium concentrations leached from MK/gasified resin samples were very low and even below detection limit in some cases. Even with the 50% dosing, leached cesium concentrations were very low from the MK/gasified resin combination.

Calculated apparent Cs diffusion coefficients are presented in Figure 1. Average apparent diffusion coefficient was 1.1×10^{-7} cm^2/s for OPC/doped resin combination. For OPC/gasified resin, the average apparent diffusion coefficient was 6.2×10^{-9} cm^2/s. Average apparent diffusion coefficients for BFS/gasified resin and MK/gasified resins were 1.0×10^{-9} cm^2/s and 1.1×10^{-12} cm^2/s, respectively. Apparent diffusion coefficients enabled calculations related to maximum encapsulated cesium contents related to released cesium content. Assuming identical cases (exposure times, geometry and leachate volumes), the dosing of initially encapsulated material becomes proportional to apparent diffusion coefficients according to Equation 2.

$$P_{eq} = \frac{A_0}{A_0^{ref}} = \sqrt{\frac{D^{ref}}{D}} \tag{2}$$

In Equation 2, P_{eq} is the proportional encapsulated resin content for equal leachate concentrations, A_0^{ref} is the total quantity of the tracer in reference sample and D^{ref} is the apparent diffusion coefficient of reference sample (cm^2/s). Table 4 presents the calculated proportional encapsulated resin contents for equal cesium leachate concentrations. On average, gasification of the resin enabled five times more cesium to be included within the OPC matrix. With BFS and MK -binders, gasification of the resin enabled 9 and 800 times more cesium in the samples.

Table 3. Measured leachate concentrations from short-term leaching test procedure. Dosing corresponds to the amount of pristine resin.

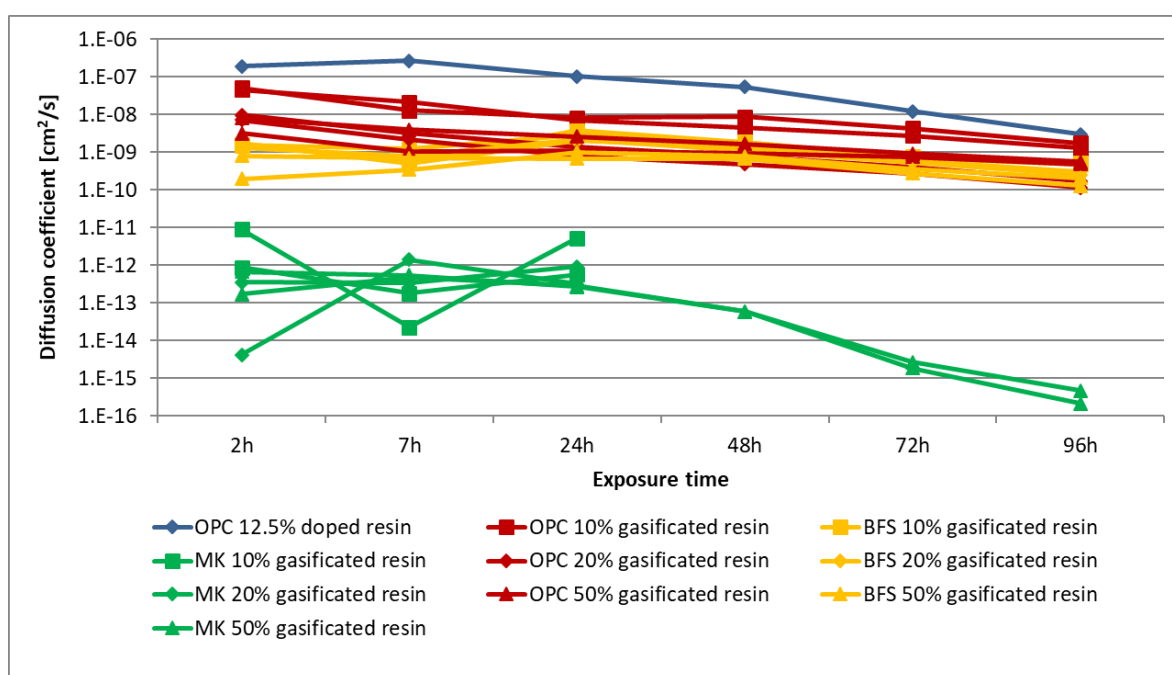| Binder system		Dosing /%	Leachate concentrations (ppb)					
			2h	7h	24h	48h	72h	96h
OPC	doped resin	13	4.53	4.07	4.65	4.32	2.35	1.31
OPC	gasified resin	10	1.53	1.10	1.38	1.60	1.35	1.01
BFS	gasified resin	10	0.32	0.29	1.06	1.00	0.73	0.67
MK	gasified resin	10	0.01	0.00	0.02	[a]	[a]	[a]
OPC	gasified resin	20	1.41	0.97	1.13	1.11	0.93	0.67
BFS	gasified resin	20	0.72	0.57	1.92	1.89	1.47	1.17
MK	gasified resin	20	0.00	0.01	0.02	[a]	[a]	[a]
OPC	gasified resin	50	4.26	3.43	5.53	5.97	5.60	4.94
BFS	gasified resin	50	1.43	1.86	4.40	5.24	3.98	3.25
MK	gasified resin	50	0.03	0.04	0.06	0.04	0.01	0.00

[a] Under detection limit.

Figure 1. Calculated apparent Cs diffusion coefficients from short-term leaching test procedure.

Table 4. Calculated proportional initial cesium contents for equal cesium leachate concentrations.

Binder system		Dosing /%	Proportional encapsulated resin contents (P_{eq})					
			2h	7h	24h	48h	72h	96h
OPC	doped resin	13	1	1	1	1	1	1
OPC	gasified resin	10	2	3	4	3	2	1
BFS	gasified resin	10	11	15	6	5	4	2
MK	gasified resin	10	198	1361	188	-	-	-
OPC	gasified resin	20	5	8	10	9	6	5
BFS	gasified resin	20	11	17	7	7	5	3
MK	gasified resin	20	1036	469	406	-	-	-
OPC	gasified resin	50	6	9	7	6	4	2
BFS	gasified resin	50	20	19	11	9	6	4
MK	gasified resin	50	672	609	607	963	2305	2958

Compression strength results are presented in Figure 2. Compression strength of the samples decreased as the amount of pristine resin in the samples increased whereas with gasified resin, such a behaviour was not observed.
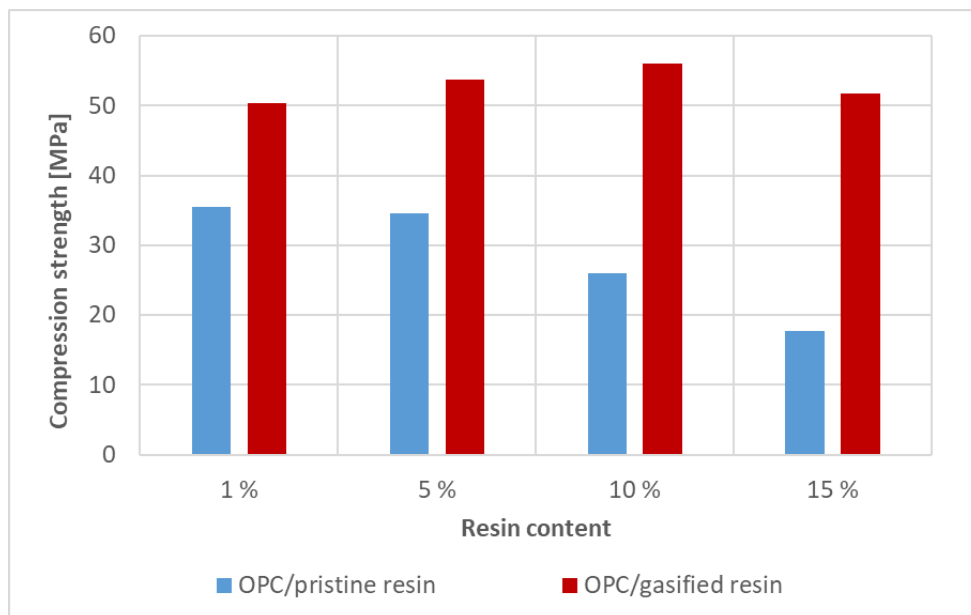
Figure 2. Compression strengths of the OPC/pristine resin, OPC/gasified resin.

4. Discussion

The United States Nuclear Regulatory Commission has defined a limit for leachability of solidified low-level radioactive wastes by a short-term test procedure. Materials with average apparent diffusion coefficients lower than 10^{-6} cm^2/s are suitable for encapsulation of low-level radioactive waste. Each studied material combination fulfilled the boundary limit requirement.

According to our results, gasification of IXR is a beneficial technique with respect to apparent diffusion coefficients and compression strengths. Average apparent diffusion coefficients decreased when the resin was gasified. If the OPC binder was - replaced with BFS or MK, the decrease was even greater. According to calculations, MK matrix and gasified resin enabled incorporation of almost 800

times more cesium in the sample, compared to traditionally used OPC/pristine resin combination. Addition of gasified resin did not decrease the compression strength of the samples within the studied range. Compression strength has been a limiting factor with pristine resin.

The maximum dosing of the gasified resin was not defined in this study. It remained unclear what would be the limiting factor for developed encapsulation system. Theoretically, limiting factors could be one of the following:

- Apparent diffusion coefficient
- Mechanical properties
- Radioactivity

Apparent diffusion coefficient will become a limiting factor at some point. According to calculations, such point will be around 5 times higher dosing in OPC matrix, 9 times in BFS and 800 times in MK.

Compression strength studies did not present decrease in compression strength up to 15% dosing of gasified resin, which is in region of the proposed dosing. It is likely that mechanical properties will not be the limiting factor for gasified resins within the studied range. Radioactivity of the encapsulated samples would increase similarly to the dosing. It is possible that increasing the activity of the sample by 800 times could change the wastes classification from LILW to HLW.

Although the ultimate limits for the studied system was not achieved, two interesting points were studied. First point is the dosing corresponding to cesium content 35% of pristine resin where the Cesium dosing corresponds to cesium content of IXR in the bulk density. According to results, MK encapsulation generated Cs leachate concentrations below those measured with OPC/pristine resin. Another interesting point was cesium content corresponding to 50% of pristine resin. Encapsulation to solid glass phase via melting has typically pristine resin content of 50%. MK matrix enabled gasified resin corresponding to 50% pristine resin content. Compression strength of the sample was good and Cs leachate concentrations were below those obtained for conventional OPC/pristine resin wasteforms.

5. Conclusions

This study demonstrated that gasification of the IXR would be a beneficial treatment to reduce the total volume of LILW requiring disposal. Encapsulation of gasified resin increased sample's compression strength and reduced the apparent diffusion coefficient of Cs tracer compared to pristine resin sample. Changing the binder from OPC to BFS or MK reduced apparent diffusion coefficient even further. Specifically, the use of MK decreased the rate of Cs diffusion from the sample and some of the leachate concentrations were even below detection limit. Calculated average apparent diffusion coefficients enabled comparison of the encapsulated Cs content assuming identical leachate concentrations. According to calculations, use of the MK matrix would enable 800 times higher initial Cs concentration compared to conventional OPC/pristine resin encapsulation matrices.

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