

# 1 Low pH Concrete for Use in a US High-Level Waste Repository: Part II—Formulation and Tests

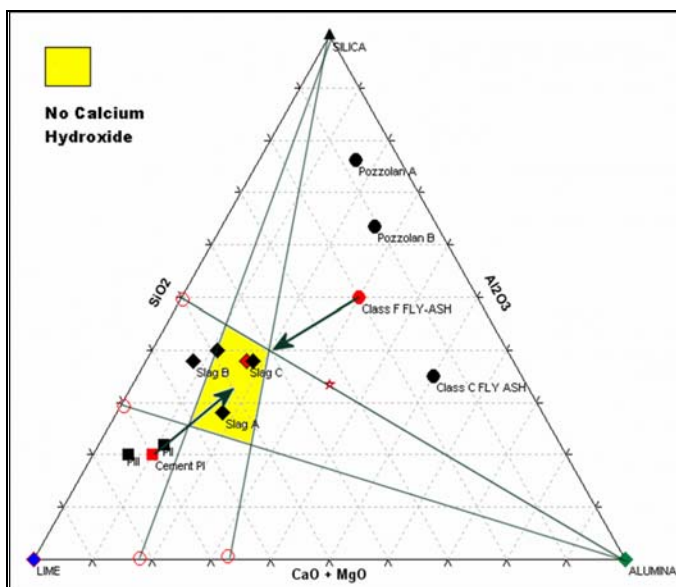
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## 1.1 Introduction

Because of the cost savings, concrete may be considered for the construction of the tunnels and drifts in the repository<sup>1,2</sup> in the second-generation design of the proposed Yucca Mountain Project (YMP) repository. In order for a concrete to be accepted for use in the Yucca Mountain (YM) repository, it must be shown that leachates from the concrete do not increase the mobility of uranium and that it is durable under the expected service conditions of the disposal drifts. In an ordinary concrete binder, Portlandite ( $\text{Ca}(\text{OH})_2$ ) is formed. It is the most soluble phase of Portlandite and results in a high pH. Therefore, preparing a concrete with the smallest possible amount of Portlandite improves its durability and mitigates potential impacts on the transport of uranium from the repository. A team from Penn State University<sup>3</sup> generated a ternary diagram of the main cement constituents— $\text{CaO}$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ —that shows ranges of composition in which Portlandite is not formed. This composition field is shown as yellow in Figure 1-1.

From major suppliers in the southwestern region of the United States, we obtained samples of their products, and data showing their full characterization. From Lafarge North America, we chose a type V ordinary Portland cement (V-OPC), a ground granulated blast furnace slag (BFS), and silica fume (SF). We obtained a class F fly ash (FA) from Headwaters Resources. Degussa provided the organic superplasticizer Glenium 3030NS.

The coarse aggregate was basalt produced by Martin Marietta Aggregates in their facility at Mountain Quarry in Oroville, California; the sand was feldspar, containing mostly silica, and was obtained from PW Gillibrand Sand and Gravel Mine, in Simi Valley, California. Finally, metal fibers from the Bekaert Group were selected for micro-reinforcement of the concretes.



**Figure 1-1. Ternary diagram showing the compositions with no Portlandite.**

## 1.2 Selection of the Dry Blend Composition and Methodology

Preliminary tests were performed to verify that the limits indicated in Figure 1-1 were relevant for the selected materials. Ten mixes were prepared with the amount of V-OPC varying from 20 to 100%, the amount of BFS varied from 0 to 50%, and the amount of FA varied from 0 to 35%. SF was not added in this first series. For accelerating the reactions, a small amount (4 g) of dry mix— OPC, BFS, and FA— was mixed constantly with a large amount of water (40 mL). The total composition of the dry mix was based on the chemical data for each additive and the total composition for CaO+MgO, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> and was blended to not form Portlandite. Four samples were prepared for each mixture, one for each of the time intervals selected— 10, 30, 58 and 70 days. A second series of tests was performed with SF. After each period, the aqueous phase was removed for inductively coupled argon plasma (ICP) analysis (Thermo Jarrell Ash 61E Trace), and the solutions' pH were also measured.

The solid phases were dried at 80°C until constant weight was achieved. Since the tests were only for scoping purpose, no special precautions were taken to minimize the effect of CO<sub>2</sub>. In the solid phase, the content of Portlandite had to be measured, but because of the large number of samples, thermogravimetric analyses were performed only on a few selected samples that were then used as calibration standards for the measurements made by X-ray diffraction (XRD). The thermogravimetric and differential thermal analysis (TGA/DTA) instrument was a Harrop Model ST-736.

In the TGA analysis, the sample was heated in 6 h to a temperature of ~900°C. The weight loss occurring in the 430–530°C range, which is caused by the loss of water from the calcium hydroxide, was measured and represented the amount of Portlandite present in the sample. Another aliquot of the sample was mixed with 10% of silicon powder, serving as an internal standard for the measurements by XRD. The XRD analyses were performed using a Scintag PADV vertical  $\theta/2\theta$  goniometer. The area under the peak at 18°(2- $\theta$ ) was used for Ca(OH)<sub>2</sub> while the peak at 28.5° was used for the internal standard (Si). The ratios of the areas Ca(OH)<sub>2</sub>/Si were calculated and tabulated against the results obtained by thermogravimetry. A correlation curve was created and used for measuring the Ca(OH)<sub>2</sub> content of all the samples. The results obtained are found in Table 1-1 for the mixes without silica fume and Table 1-2 for those with silica fume added.

In the cases with SF, these results show those formulations containing 30 to 50 wt % of Portland cement with a combination of admixtures, which could result in very little or no Portlandite. Having established the control and elimination of free calcium hydroxide, the physical and civil engineering characteristic must also be verified to ensure that these formulations could provide sufficient strength for building and supporting the tunnels infrastructure.

<b>Table 1-1. Evolution of the Portlandite content in the mixes without silica fume</b>				
<b>Mix name</b>	<b>% by weight Ca(OH)<sub>2</sub> present in the mix</b>			
	<b>10 days</b>	<b>32 days</b>	<b>53 days</b>	<b>68 days</b>
<b>A-20%(OPC)-50%(BFS)-30%(FA)</b>	0.279	0.027	0.020	0
<b>B-25%(OPC)-40%(BFS)-35%(FA)</b>	0.341	0.204	0.0027	0
<b>C-30%(OPC)-35%(BFS)-35%(FA)</b>	0.750	0.477	0.273	0.068
<b>D-35%(OPC)-40%(BFS)-25%(FA)</b>	0.832	0.818	0.205	0.205
<b>E- 35%(OPC)-30%(BFS)-35%(FA)</b>	0.477	0.545	0.205	0.136
<b>F-40%(OPC)-30%(BFS)-30%(FA)</b>	1.022	1.159	0.409	0.682
<b>G-45%(OPC)-25%(BFS)-30%(FA)</b>	1.977	1.159	0.920	0.818
<b>H-50%(OPC)-25%(BFS)-25%(FA)</b>	1.295	2.727	0.750	0.614
<b>I-55%(OPC)-20%(BFS)-25%(FA)</b>	2.658	1.977	0.954	1.363
<b>J-60%(OPC)-10%(BFS)-30%(FA)</b>	2.590	2.386	1.023	1.363
<b>V-100%(OPC)-0%(BFS)-0%(FA)</b>	3.476	6.748	4.158	4.022

<b>Table 1-2. Evolution of the Portlandite present in the mixes with silica fume</b>				
Mix name	% by weight Ca(OH) <sub>2</sub> present in the mix			
	10 days	33 days	53 days	70 days
<b>BB-25%(OPC)-40%(BFS)-30%(FA)-5%(SF)</b>	0.491	0.000	0.000	0.000
<b>CC-30%(OPC)-35%(BFS)-30%(FA)-5%(SF)</b>	2.031	0.061	0.000	0.000
<b>DD-35%(OPC)-40%(BFS)-20%(FA)-5%(SF)</b>	0.504	0.109	0.000	0.000
<b>EE-35%(OPC)-30%(BFS)-30%(FA)-5%(SF)</b>	0.423	0.382	0.000	0.000
<b>FL-40%(OPC)-30%(BFS)-25%(FA)-5%(SF)*</b>	0.593	0.307	0.198	0.000
<b>FH-40%(OPC)-30%(BFS)-22%(FA)-8%(SF)</b>	0.491	0.102	0.034	0.000
<b>GL-45%(OPC)-25%(BFS)-25%(FA)-5%(SF)</b>	0.961	0.682	0.341	0.307
<b>GH-45%(OPC)-25%(BFS)-22%(FA)-8%(SF)</b>	0.450	0.436	0.225	0.055
<b>HL-50%(OPC)-25%(BFS)-20%(FA)-5%(SF)</b>	0.532	0.382	0.061	0.130
<b>HH-50%(OPC)-25%(BFS)-18%(FA)-8%(SF)</b>	0.457	0.239	0.191	0.239
<i>* Mixture selected for use in future testing of concretes for inverts and shotcrete.</i>				

### 1.3 Tests of Mortars with Different Compositions

To confirm that these formulations produced enough early compressive strength to allow its use in the construction of the tunnel liners, tests of sand mortars were done following American Society for Testing and Materials (ASTM) C109. Five mixes containing 30 to 50% Portland cement with various amount of fly ash, blast furnace slag, and silica fume were prepared. The compositions and the compressive strengths that developed are shown in Table 1-3. This data shows that after 3 months of curing, all the mixes tested achieved 32 MPa or higher.

<b>Table 1-3. Composition by weight percent and properties of the sand mortars tested</b>					
	<b>30%(OPC)- 35%(BFS)- 30%(FA)- 5%(SF)</b>	<b>35%(OPC)- 40%(BFS)- 20%(FA)- 5%(SF)</b>	<b>40%(OPC)- 30%(BFS)- 25%(FA)- 5%(SF)</b>	<b>45%(OPC)- 25%(BFS)- 25%(FA)- 5%(SF)</b>	<b>50%(OPC)- 25%(BFS)- 20%(FA)- 5%(SF)</b>
Type V (g)	120	140	<b>160</b>	180	200
BFS (g)	140	160	<b>120</b>	100	100
FA (g)	120	80	<b>100</b>	100	80
SF (g)	20	20	<b>20</b>	20	20
Dry blend (g)	400	400	<b>400</b>	400	400
Wet sand (g)	1176	1176	<b>1176</b>	1176	1176
Water (g)	145	145	<b>145</b>	145	145
Glenium 3030NS (mL)	1.5	0	<b>1.5</b>	2.5	2
<b>Compressive strength (MPa)</b>					
3 days	6.9 +/- 1.0	8.3 +/- 0.7	<b>9.0 +/- 0.7</b>	8.3 +/- 0.7	9.1 +/- 0.7
7 days	14.1 +/- 0.7	17.6 +/- 0.7	<b>16.9 +/- 1.0</b>	15.9 +/- 0.7	16.6 +/- 0.7
14 days	23.4 +/- 1.4	25.5 +/- 1.4	<b>25.9 +/- 1.4</b>	25.9 +/- 1.0	27.6 +/- 0.7
28 days	31.0 +/- 1.4	23.1 +/- 1.0	<b>30.7 +/- 1.0</b>	33.4 +/- 1.0	36.9 +/- 1.7
2 months	28.6 +/- 2.1	29.0 +/- 1.4	<b>34.5 +/- 1.7</b>	37.6 +/- 1.4	41.4 +/- 1.0
3 months	33.1 +/- 3.4	32.4 +/- 2.1	<b>38.3 +/- 1.7</b>	40.7 +/- 2.1	42.1 +/- 1.0

These proportions made mortars with very good strength and prevented the formation of free hydroxide, mitigating the potential mobilization of uranium and improving the concrete's durability under repository service conditions. Based on the chemical analyses and strength, cementitious blend

FL (40% OPC-30% BFS -25% FA -5% SF) was chosen for further testing in the concrete formulations of the inverts and shotcrete. This formulation allowed a low calcium hydroxide content during early curing in order to allow etching of the fine and coarse aggregates for improved aggregate binder adhesion, while completely eliminating free hydroxide after 70 days.

## 1.4 Preparation of the micro concrete specimens

Based on these results, a formulation for the shotcrete was proportioned by a consultant, Mr. Peter Tatnall of Performance Concrete Technology (PCT) to comply with current ASTM and American Concrete Institute (ACI) guidelines. This proportioned shotcrete mix is shown in Table 1-4.

Table 1-4. Formulation proportions selected for the shotcrete						
Ingredient	lbs/yd	Specific gravity	ft <sup>3</sup> /yd <sup>3</sup>	kg/m <sup>3</sup>	%	
Cement— type V	290	3.15	1.475	172	40.0	by mass
Blast furnace slag (BFS)	219	2.93	1.198	130	30.2	by mass
Fly ash— type F (FA)	182	2.32	1.257	108	25.1	by mass
Silica fume (SF)	34	2.31	0.236	20	4.7	by mass
<b>Total cementitious materials</b>	<b>725</b>		<b>4.166</b>	<b>430</b>	<b>15.4</b>	by vol.
Water	326	1.00	5.224	193	0.45	by mass
Steel fibers	101	7.85	0.206	60	0.76	by vol.
Air @ 1%		0.01	0.270			
Fine aggregate— Gillibrand sand	1993	2.62	12.188	1183	45.0	by vol.
Coarse aggregate—Martin Marietta basalt	919	2.82	5.223	545	19.3	by vol.
Admixtures— Glenium 3030 NS	1.75	1.00	0.028	1		
<b>Total concrete</b>	<b>4065</b>		<b>27.100</b>	<b>2413</b>		

The same proportions of each of the constituents presented in Table 1-4 were used for preparing the micro specimens. The mixing was performed in a Hobart mixer, following the practice described in ASTM C305. Small specimens were needed for the laboratory durability tests (Figure 1-2). These specimens were cast in vials with a volume of 4 mL and a diameter of 11 mm. The sizes of the aggregates were reduced: the sand fractions used were finer than 1.4 mm, and the basalt was crushed and sieved to 1.4–3.5 mm fractions. A cross section of a specimen is shown in Figure 1-4.



Figure 1-2. Micro concrete specimen ( $h \approx 2$  cm).



Figure 1-3. Vessels used in the experiment.

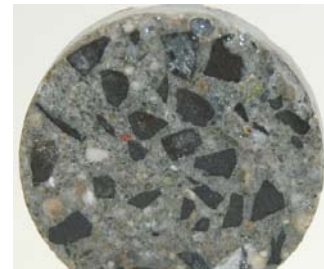


Figure 1-4. Transverse 11 mm section of a specimen.

## 1.5 Exposure to a groundwater surrogate from Yucca Mountain

The exposure of the micro concrete specimens was performed at three temperatures: room temperature, 90°C (average temperature the concrete is supposed to be submitted to) and 170°C (maximum temperature the concrete could be submitted to). The set up and equipment were already used in a previous project<sup>4</sup>(Figure 1-3). A ratio of 4 volumes of Yucca Mountain surrogate to one surface area of micro concrete specimen was selected for being compatible with the equipment. Two surrogates of different ionic strengths were used: one was derived from a composite of groundwaters from the J13 well and the unsaturated zone (UZ) of Yucca Mountain. In this report the synthetic brines are designated  $\times 1YM$  and  $\times 10Y$ . The exposures were 1, 3, 6, and 9 months. Some tests exposed surrogates to a specimen of concrete only, other tests added a pellet of high-fired, spent fuel made of depleted  $UO_2$  (Figure 1-5). Reference tests were performed, some using only a pellet of  $UO_2$  and others using blanks containing only brines. After each interval, the solutions were analyzed for metals content by ICP-AES, the pH was measured, a titration was performed for carbonate-bicarbonate speciation and the anions. The solids specimens were dried and examined by scanning electron microscopy (SEM) to follow the alterations in the microstructure.



*Figure 1-5. Pellets of high-fired  $UO_2$ .*

<b>Table 1-5. Composition of the <math>\times 10</math> YM surrogate solution</b>		
	<b>Target <math>\times 10</math> YM (mg/L)</b>	<b>Actual* surrogate <math>\times 10</math> YM (mg/L)</b>
<b>pH</b>		8.2 to 8.4
<b>[Ca]</b>	650	160
<b>[Mg]</b>	120	151
<b>[K]</b>	50.4	83
<b>[Na]</b>	458	875
<b>[Si]</b>	13.69	10.2
<b>[Sr]</b>	-	0.13
<b>[Cl]</b>	770	650
<b>[SO<sub>4</sub>]</b>	790	900
<b>[NO<sub>3</sub>]</b>	120	374
<b>[OH]</b>	-	0
<b>[CO<sub>3</sub>]</b>	-	2.9
<b>[HCO<sub>3</sub>]</b>	1289	547
* Actual compositions vary from the target concentrations because the solutions are unstable at the target concentrations.		

## 1.6 Results from the Exposure Test

At the time of this paper, specimens have been exposed for 9 months. Characterizations of the liquid phases were performed, as well as scanning electron microscopy. Deposits were observed on several concrete and  $UO_2$  specimens (Figures 1-6 and 1-7). The pH values are reported in Table 1-6.



*Figure 1-6. The concrete in  $\times 10$  YM.*



*Figure 1-7. The concrete in  $\times 1$  YM.*

<b>Table 1-6. Evolution of pH with time</b>						
	<b>Test code</b>	<b>t<sub>0</sub></b>	<b>1 month</b>	<b>3 months</b>	<b>6 months</b>	<b>9 months</b>
<b>Initial solution ×1 YM</b>	1YM	8.41				
<b>Initial solution ×10 YM</b>	10YM	8.4				
<b>20°C- concrete -1YM</b>	<b>20C (1YM)</b>	-	11.83	11.77	11.94	11.97
<b>20°C- concrete + UO<sub>2</sub> -1YM</b>	<b>20U (1YM)</b>	-	11.83	11.65	11.37	11.81
<b>90°C- concrete -1YM</b>	<b>90C (1YM)</b>	-	11.49	11.46	11.01	10.98
<b>90°C- concrete + UO<sub>2</sub> -1YM</b>	<b>90U (1YM)</b>	-	11.39	11.62	10.77	11.37
<b>90°C- UO<sub>2</sub> -1YM</b>	<b>90UO<sub>2</sub> (1YM)</b>	-	2.57	5.95	5.72	6.44
<b>170°C- concrete -1YM</b>	<b>170C (1YM)</b>	-	7.74	8.05	7.70	8.22
<b>170°C- concrete + UO<sub>2</sub> -1YM</b>	<b>170U (1YM)</b>	-	9.7	8.43	8.58	9.43
<b>170°C- UO<sub>2</sub> -1YM</b>	<b>170UO<sub>2</sub> (1YM)</b>	-	3.91	7.52	5.54	5.21
<b>20°C- concrete -10YM</b>	<b>20C (10YM)</b>	-	9.94	10.27	10.32	10.32
<b>20°C- concrete + UO<sub>2</sub> -10YM</b>	<b>20U (10YM)</b>	-	9.68	9.41	9.06	10.06
<b>90°C- concrete -10YM</b>	<b>90C (10YM)</b>	-	9.99	10.08	9.29	9.58
<b>90°C- concrete + UO<sub>2</sub> -10YM</b>	<b>90U (10YM)</b>	-	9.93	9.35	8.39	9.56
<b>90°C- UO<sub>2</sub> -10YM</b>	<b>90UO<sub>2</sub> (10YM)</b>	-	7.94	7.91	8.35	9.16
<b>170°C- concrete -10YM</b>	<b>170C (10YM)</b>	-	8.40	7.80	7.85	9.49
<b>170°C- concrete + UO<sub>2</sub> -10YM</b>	<b>170U (10YM)</b>	-	9.45	8.70	7.88	8.82
<b>170°C- UO<sub>2</sub> -10YM</b>	<b>170UO<sub>2</sub> (10YM)</b>	-	8.64	7.65	7.89	7.00

The pH of the pore solution of an OPC without additives is about 12.6. The results obtained show that the pH varies with the salt concentration and temperature. The presence of UO<sub>2</sub> shows little influence on the pH. Figure 1-8 illustrates the variation of the composition of calcium, silicon, and uranium with time for the 1-YM and 10-YM solutions. These elements are reported in milligrams of the element per gram of concrete, except for uranium, which is expressed in milligrams of uranium per gram of UO<sub>2</sub>. The release of uranium depends upon the ionic concentration of the solution. When the uranium pellet is subjected to a moderate ionic strength solution (1 YM) without concrete, the release of uranium in the solution is ten times higher than when concrete is present at a temperature of 90°C. At 170°C, the presence of concrete reduces the solubility of uranium by 100, as shown in Table 1-7.

<b>Table 1-7. Release of uranium after 6 months of exposure expressed in milligrams of uranium per gram of UO<sub>2</sub> in the pellet</b>		
<b>Conditions of exposure</b>	<b>×1 YM</b>	<b>×10 YM</b>
20°C* – concrete + UO <sub>2</sub> ( <b>20U</b> )	1.7E-03	6.7E-03
90°C – concrete + UO <sub>2</sub> ( <b>90U</b> )	2.2E-03	6.5E-03
90°C – UO <sub>2</sub> alone ( <b>90UO<sub>2</sub></b> )	2.4E-02	1.4E-02
170°C – concrete + UO <sub>2</sub> ( <b>170U</b> )	2.5E-03	4.7E-03
170°C – UO <sub>2</sub> alone ( <b>170UO<sub>2</sub></b> )	7.7E-01	1.3E-02
* Fuel pellet blank with only high-fired UO <sub>2</sub> was not available.		

After 6 months, the SEM showed that the uranium pellets' surfaces showed etching in the x10-YM solution at 170°C (Figure 1-9). With this low-pH concrete, the uranium pellets formed a protective layer, as shown in Figure 1-10. This layer contained magnesium, silicon, calcium, and uranium. This observation corroborated the chemical analysis of the leachate solutions showing order of magnitude reductions in uranium solubilities through adsorption or solubility controlling phases.

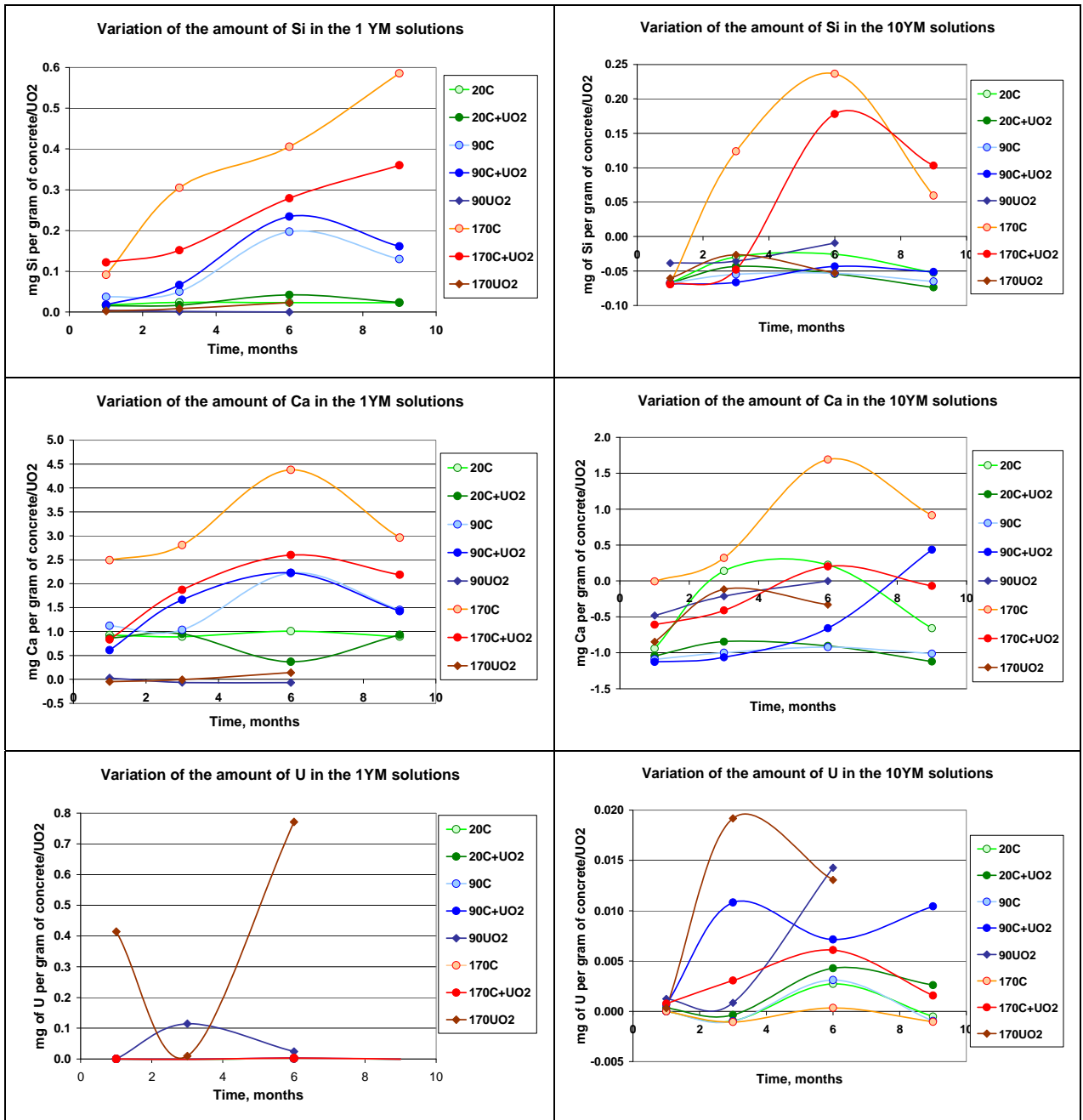
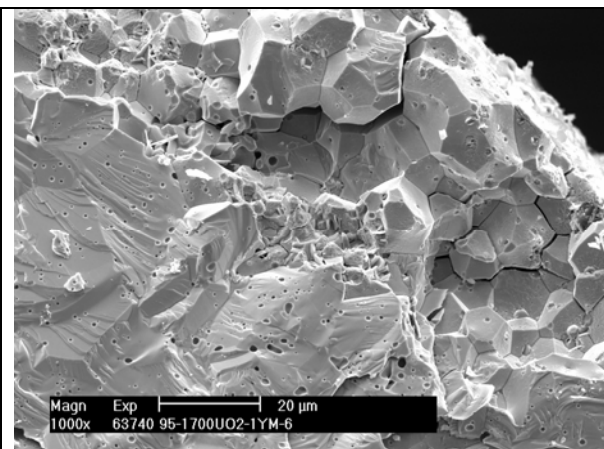


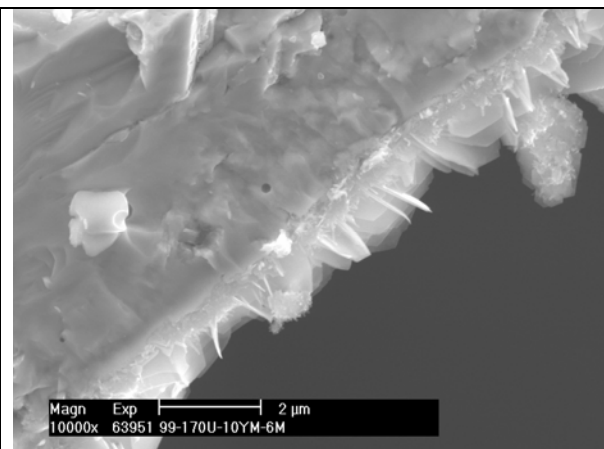
Figure 1-8. Evolution of the concentration of calcium, silicon and uranium.

## 1.7 Conclusions

The results show that these concrete formulations, using these silica admixtures, suppress the formation of free calcium hydroxide. The pH levels of the pore solutions are lowered, and the leachable silicates greatly reduce the uranium in solution. The results obtained show that the presence of this concrete protects the uranium oxide. So far, no interactions between the cement paste and aggregates have been observed, indicating long-term durability under the service conditions of the repository.



*Figure 1-9. Alteration of the UO<sub>2</sub> pellet after 6 months at 170°C in x10YM. The altered zone is ~40 μm thick.*



*Figure 1-10. Presence of a protective layer (Ca-Mg-Si) covering the UO<sub>2</sub> pellet in the presence of concrete (170°C, x10YM, 6 m).*

## 1.8 References

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- 2 **BCAA00000-01717-0200-00013 REV 00**, Sections 6.2.1- 6.2.2, "Evaluation of Alternative Materials for Emplacement Drift Ground Control, pp. 7–8 (referring to greater peak 10,000 year doses, Table 6-1).
- 3 **Roy, D. M. and B. E. Scheetz. 1992.** "The Chemistry of Cementitious Systems for Waste Management: The Penn State Experience." Chapter 3, *Chemistry and Microstructure of Solidified Waste Forms*, Ed. R.D. Spence, Lewis Publishers, Ann Arbor, MI, pp. 83–101.
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