



Study of the Main Properties and Leach Behavior of Simulated MCCI Products

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Abstract

The solidified product of melted core and concrete interaction (MCCI) was formed at the Fukushima NPP (1F), where the severe accident took place in March, 2011. In this study the structure, properties and leaching behavior of simulated MCCI samples has been performed. The solid model samples containing 40-70 wt. % of concrete components, (U,Zr)_xO_y and metallic (Cr, Ni, Fe) additives were obtained using induction melting in cold crucible (IMCC) at 2200-2500 °C. The ratio of amorphous and crystalline phases as well as their composition has been evaluated. It was shown that initial structure of samples represented mainly amorphous silicate based matrix, in which crystalline solid solutions (U,Zr)_xO_y, Fe-Cr-Ni spinel and cristobalite (SiO₂) were dispersed. Leach tests of previously characterized samples has been performed using deionized and nitride water with different pH = 4.01, 6.50, and 9.18 at temperature 25, 50, 90 and 120 °C with exposure time till 84 days. Leaching kinetics was studied and composition of the secondary phases were detected. It was set that dissolution of silicate based phase was started at 25 °C in deionized and nitride water forming secondary phases on the surface. Contrarily, such elements as U and Zr were detected in the solution only after 54 days leaching at 120 °C. As a result of such severe condition the continuous surface layers from sedimental secondary phases were obtained and analyzed.

Keywords: Aging in Aqueous Solutions; Corium; Fukushima-Daiichi NPP; Leaching Rates; Molten Core Concrete Interaction Products (MCCI); Secondary Phases; Solid Solutions of Uranium and Zirconium Oxides; Structure

Introduction

After 10 years beyond design basis accident at the Fukushima Daiichi NPP (1F) the chemical and mechanical properties of solidified ex-vessel corium debris, representative product MCCI, are not well known [1, 2].

During tests in the Colima experimental facility ex-vessel corium, containing refractory oxides (UO₂, ZrO₂), steel and components of concrete (SiO₂, Al₂O₃, CaO, Fe₂O₃), has been obtained. Experimental study of the different samples set on heterogeneous nature of them. Phase composition, microstructure of product, leaching rates also were investigated [3-6].

Nevertheless, from the point of debris defueling besides the physical and chemical properties of MCCI products, the amount of concrete erosion and formation of altered surface layers is important information.

The main goal of our study was to gain leaching data and morphology of altered layers as well as chemical composition of minerals deposited on their surface.

Experimental Part

Preparation of simulated MCCI products

For this study three simulated MCCI products representative different core-concrete ratio were selected in accordance with thermodynamic evaluation in [7].

Chemicals for batch preparation were taken in form pure oxides NiO, Cr₂O₃, FeO, SiO₂, Al₂O₃ and ZrO₂. Calcium was added in form preliminary synthesized compound CaZrO₃. Nuclear depleted uranium dioxide (UO₂) was used after grinding of the tablets till fraction less than 2 mm.

All three batches after mixing of the chemicals in needed proportion were thoroughly blended and melted in the IMCC [8].

Metallic zirconium was used as a starting material for initial inductive heating of the batches.

After heating up to 2200-2500 °C under nitrogen atmosphere and aging ~20 minutes the melt was cooled with middle rate 3-4 °C/sec. As a result, the solidified ingots weighting in 1.5-2 kg each, were produced. One of them before and after fragmentation is shown in **Figure 1**.



Figure 1: View of ingot before and after fragmentation.

Initial characterizations

Initial characterizations has been done using several centimeters size samples in order to collect preliminary information on: density, porosity, micro Vickers hardness, microstructure, the main chemical phases and the distribution of elements between the different phases. This initial information are needed for interpreting the leaching experiments, including secondary compounds formation on the sample surfaces.

The equipment and methods used for these initial characterization are named below.

Phase analysis was performed using X-ray diffractometer (XRD) D2 PHASER (Bruker, Germany) with Cu_{Kα} radiation.

Scanning Electron Microscopy (SEM) observation coupled with Energy-Dispersive X-ray Spectroscopy (EDS) using a MIRA3 scanning electron microscope TESCAN was performed to study morphology, microstructure as well as elemental analysis.

The density and porosity measurements were made by hydrostatic weighting using analytical scales OHAUS Explorer E12140.

Micro Vickers hardness was determined using a Tinius Olsen microhardness tester at a load of 9.8 N, the loading time 10 s on the basis of 10-15 measurements of indentation prints.

Analysis of leaching solutions were performed by ICP-EOS (Perkin Elmer) PlasmaQwont mod. PQ 9000. Minimal detectable concentration of elements (U, Zr, Si, Al, Fe, Ca, Ni, Cr) was 10 µg/dm³.

Leaching protocol

The samples were weighted and surface area were measured by applying a film to the surface of the sample [9].

Leach tests were carried out using monolithical samples in accordance with MCC-1 method at 25, 50, 90 and 120 °C in aerated deionized (pH≈6.50, Eh≈50 mV) and nitrided (pH≈6.50 Eh≈ - 20 mV) water with solution renewal after 1, 3, 7, 10, 14, 21 and 28 days [10]. Solution with pH=4.01 and 9.18 were prepared using standard buffers.

Nitrided water was obtained from deionized boiled and cooled water by bubbling with rate 50 l/h highly pure nitrogen at 4-5°C through it for 4 hours. The concentration in solutions as function of time, temperature and pH for all higher listing elements were measured by ICP-EOS.

Normalized mass loss-N_L(i) g/cm² and leach rates-R_L(i) g/cm²-day were calculated according to the following formulas:

$$N_L(i) = \frac{m_i}{f_i \cdot S}; \quad (1)$$

$$R_L(i) = \frac{dN_L(i)}{dt}; \quad (2)$$

where $N_L(i)$ – normalized loss of element i , g/cm^2 ; $R_L(i)$ – leaching rate of element i , $g/cm^2 \cdot day$; m_i – mass of element i in aqueous solution, g ; S – surface area of sample, cm^2 ; f_i – fraction of element i in the sample.

Experimental Results and Discussion

Phase composition and microstructure

The three types of simulated MCCI products are shown in **Figure 2** together with data of their density and micro Vickers hardness.

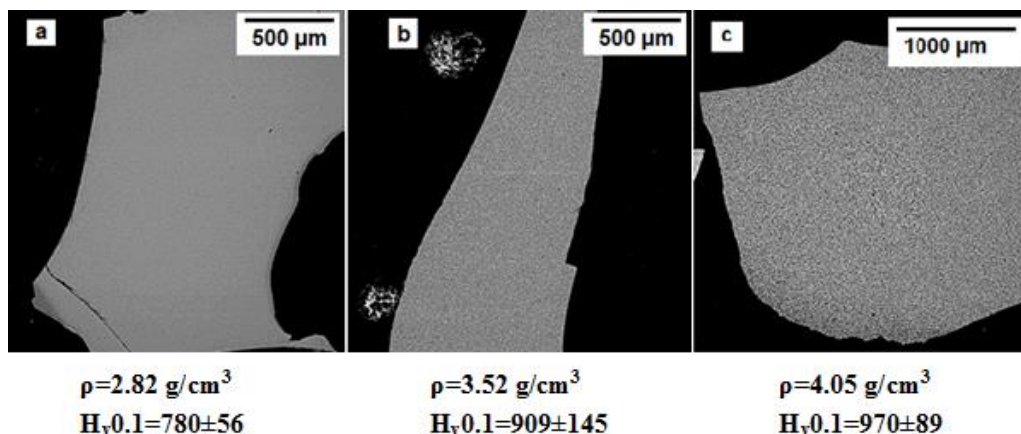


Figure 2: SEM observation for three simulated MCCI products 1 (a), 2 (b), 3 (c).

All samples represented in **Figure 2** are very dense non-porous ceramics, which bulk density and micro Vickers hardness became bigger due to higher concentration of UO_2 . There are no visible pores, which were observed in for Colima 4 test [2].

Table 1 summarize the composition of their in terms of mass percentage (wt. %), according to SEM/EDS data.

Oxide	Number MCCI product		
	1	2	3
UO_2	12.78	26.21	36.78
ZrO_2	5.56	8.84	11.78
FeO	3.01	4.31	5.45
Cr_2O_3	0.75	1.04	1.40
NiO	0.30	0.56	0.60
SiO_2	63.03	47.32	33.00
CaO	5.94	4.72	4.38
Al_2O_3	8.62	6.91	6.61
Corium : Concrete mass ratio	22:78	41:59	56:44

Table 1: Medium composition of three MCCI products (wt. %) according to SEM/EDS data (area of analysis $300 \times 300 \mu m$, measurement accuracy $\pm 2\%$).

XRD analysis data pointed to formation of a number of crystalline phases and amorphous one. Solid solutions with a stoichiometry close to $U_{0.95}Zr_{0.05}O_2$ and $Zr_{0.88}U_{0.12}O_2$ as well as spinel like $Fe(Fe,Cr,Ni)O_2$ and SiO_2 in form of cristobalite were identified. Interaction of UO_2 and ZrO_2 with concrete's additives was not detected because formation of uranium or zirconium silicates was not identified nowhere.

Microstructure, shown in **Figure 3**, illustrate the heterogeneous nature of the products under study. It can be seen from **Figure 3**, that phases, containing heavy elements (white) uniformly enough spread throughout amorphous matrix (grey).

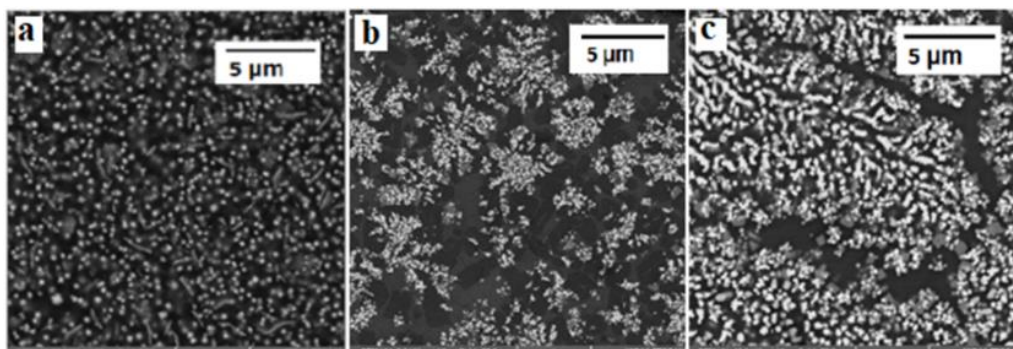


Figure 3: SEM-BSE observation for three simulated MCCI products 1 (a), 2 (b), 3 (c).

For each three MCCI products the quantitative SEM/EDS analysis was carried out on several distinct spots. Ratio of different phases, based on the obtained results, are shown in Figure 4.

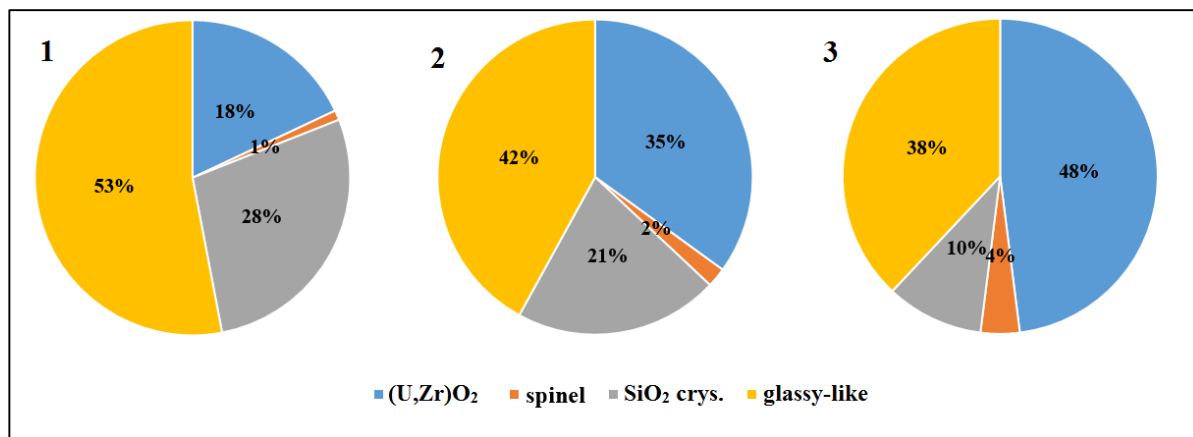


Figure 4: Ratio of phases which were formed in simulated MCCI products.

More detailed composition of the amorphous glassy-like phase in all three products are shown in Table 2, which demonstrates very close content of each chemical form everywhere.

Oxide	Number MCCI product		
	1	2	3
SiO ₂	71	70	68
CaO	12	12	13
Al ₂ O ₃	15	15	15
Spinel	2	3	4
Total	100	100	100

Table 2: Composition of glassy-like phase in MCCI products (wt. %).

As opposed to earlier data [11] silicate glassy-like phase containing dissolved uranium was not found.

Comparison of leach behavior in different conditions

Only elements from amorphous glassy-like phases (Si, Al, Ca) were detected in the leachates during tests at 25, 50 and 90 °C in deionized and nitrided water. No any amount of uranium, zirconium, nickel and chromium were found in the leachates.

Normalized weight losses of elements in total (Si, Al, Ca) and the only for calcium are shown in Figure 5.

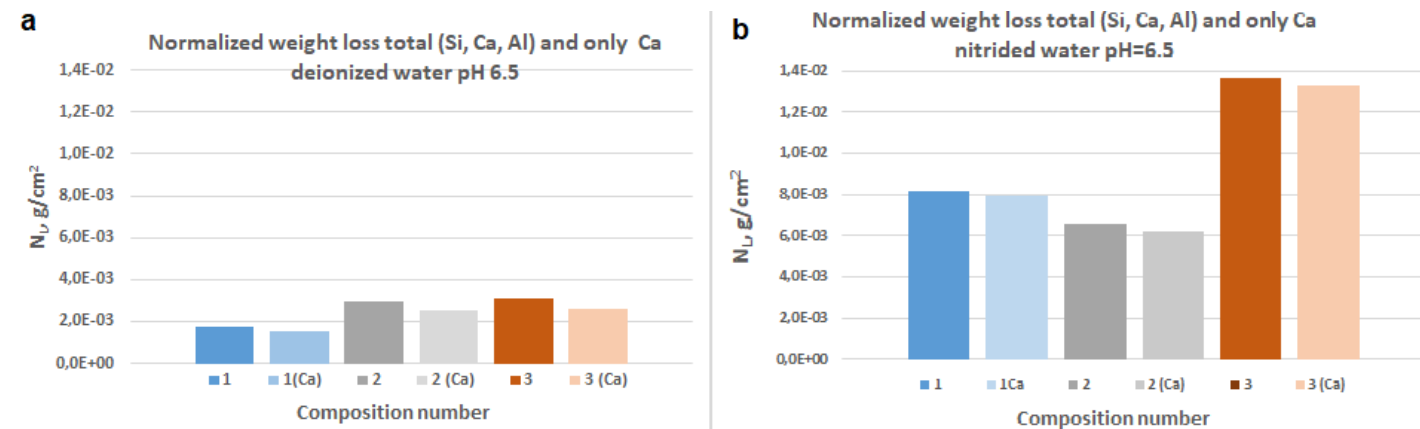


Figure 5: Total normalized losses of Al, Si, Ca and only Ca in deionized (a) and nitrided (b) water (28 days, T=90°C, pH=6.50).

As follows from **Figure 5** it could be concluded that total mass losses has very close tendency and mainly characterized by calcium leaching in the same conditions.

Altered surface layer after leach test at 90 °C for products 1, 2 and 3 in deionized water has differences in total amount. **Figure 6** demonstrates that such layer became less when amount of amorphous glassy-like phase (grey) reduces from product 1 to 3.

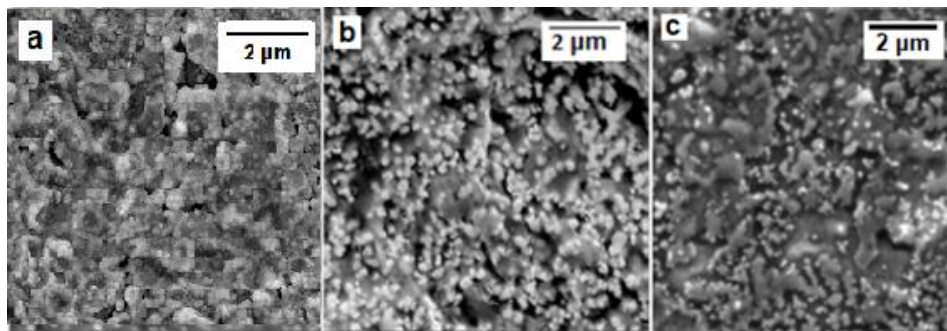


Figure 6: SEM observations of surface products 1(a), 2(b), 3(c) after leaching in deionized water (pH=6.50, 28 days, 90 °C).

Influence of pH solution on altered surface layer after 28 days at 90 °C leaching in deionized and nitride water are shown in **Figure 7**. These SEM observations clear demonstrate

the differences in morphology of altered layers, which depend on water pH and Eh.

Chemical compositions of all altered layers, according to SEM/EDS analysis are shown in **Table 3**.

pH	Oxide						Total
	Al ₂ O ₃	SiO ₂	CaO	Cr ₂ O ₃	FeO	NiO	
Deionized water (Eh≈50 mV), Product 2							
Initial	11	78	7	1	4	1	100
4.01	6	85	4	0	5	1	100
6.50	7	70	2	2	20	0	100
9.18	6	64	2	0	28	0	100
Nitrided water (Eh≈ - 20 mV), Product 1							
Initial	11	77	7	1	3	1	100
4.01	8	83	5	0	3	0	100
6.50	9	79	7	0	5	0	100
9.18	4	76	3	0	14	4	100

Table 3: Chemical composition of surface layers before initial and after leach test (pH=4.01, 6.50, 9.18, 28 days, 90 °C).

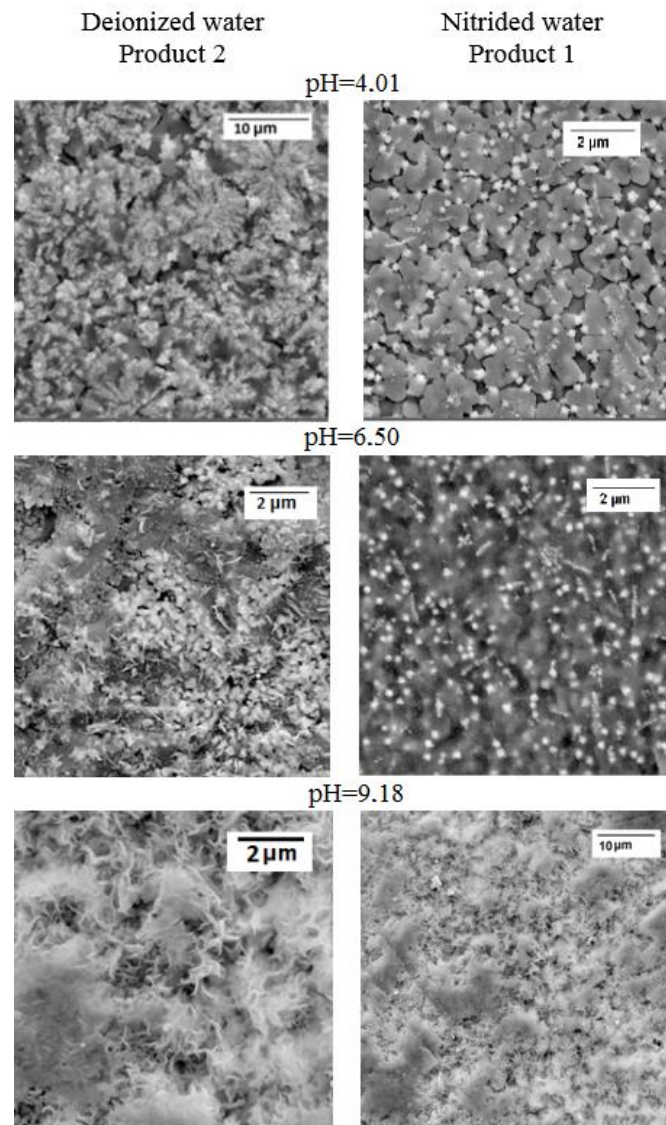


Figure 7: SEM observations of altered surface layers (pH=4.01, 6.50, 9.18; 28 days; 90 °C).

Comparison the data in **Table 3** indicates that pH value of water has more significant influence on alteration process than Eh.

The concentration of SiO₂ in layers became higher in acidic condition, while at alkaline condition its amount became less. Amount of FeO was increased, probably, due to hydrolysis.

Leach test in deionized water (pH=6.50, 56 days, 90 °C)

Total normalized mass loss for main elements (Si, Al, Ca) of amorphous glassy-like phase are shown in **Figure 8**.

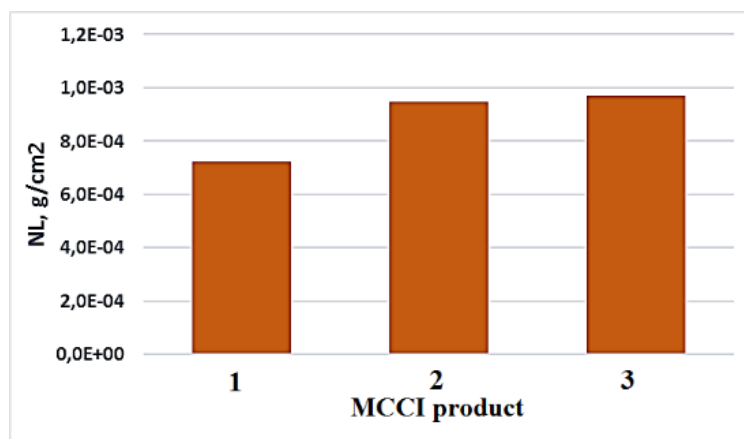


Figure 8: Summarized normalized mass loss of Si, Al, Si during 56 days in deionized water, pH=6.50, 90 °C.

Results of SEM/EDS analysis of the altered surface layers for all three product are shown in **Figure 9**.

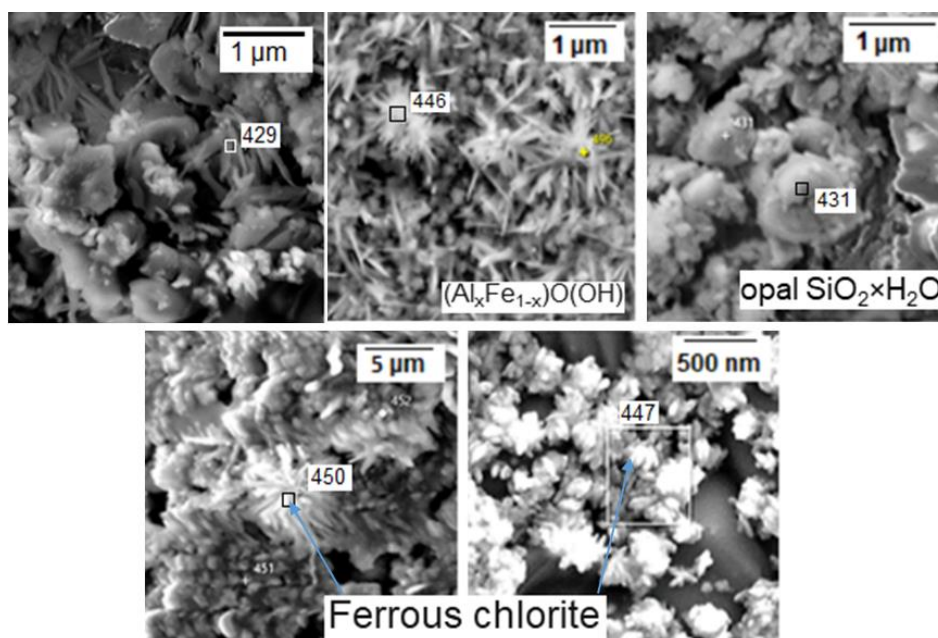


Figure 9: SEM observation of the surface after leach in deionized water (pH=6.50, 56 days, 90 °C).

Results of SEM/EDS analysis for different local spots, indicated on **Figure 9**, are presented in **Table 4**.

Spectrum number	O	Al	Si	Fe	Ni	Zr	U	Total
429	59.80	19.11	16.20	3.26	0.00	1.63	0.00	100
431	65.13	0.90	33.97	0.00	0.00	0.00	0.00	100
447	62.10	8.41	12.83	15.66	0.00	0.00	0.00	100
450	62.24	8.77	12.54	16.45	0.00	0.00	0.00	100
446	63.66	23.05	3.74	9.55	0.00	0.00	0.00	100

Table 4: SEM/EDS analysis data of secondary reprecipitated phases (at %).

The secondary reprecipitated phases, as follows from **Figure 9** and **Table 4**, could be identified as mineral formation kaolinite (spectrum 429), spherical formation of hydrolyzed silicon oxide $\text{SiO}_2 \cdot \text{H}_2\text{O}$ (spectrum 431) and extended crystals of ferrous chlorites (spectrum 447 and 450).

The secondary reprecipitated phases containing any amount of uranium or zirconium were not observed at these conditions.

Leach behavior of the products under hydrothermal condition

Leach test under hydrothermal condition has duration of 84 days at 120 °C. Deionized water with pH=6.50 was used. At these hard conditions even uranium and zirconium were detected in leachates, but in different time of renewal water. So, zirconium was founded after 49 days, while uranium only after 56 days.

Figure 10 demonstrates leach rates for concrete (Si, Ca, Al) and core (U, Zr) components.

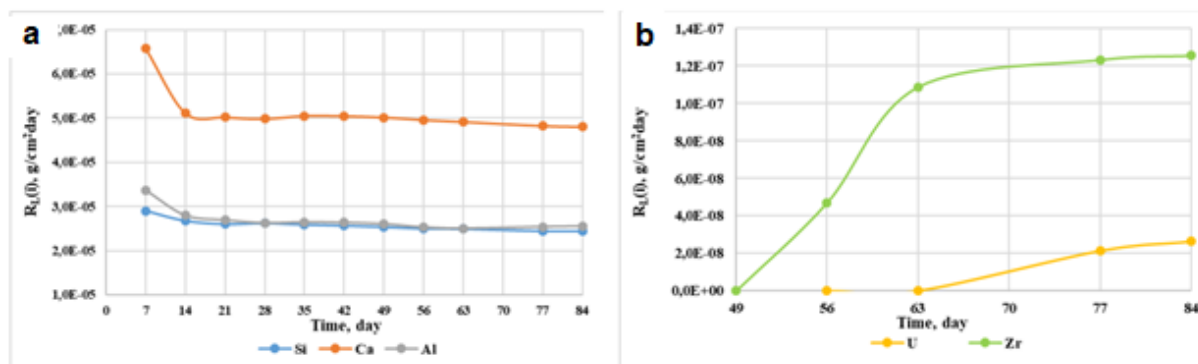


Figure 10: Dependence of the leaching rate of Si, Ca, Al (a) and U, Zr (b) on time for product 2.

The common tendency of leaching at the named hard condition to keep the same character as could be seen before. Maximum value belong to calcium, but silicon and aluminum have leach rates less by factor of two, approximately. Leach rates of zirconium and uranium after 84 days were equal $1.26 \cdot 10^{-7}$ and $3.47 \cdot 10^{-7}$ $\text{g/cm}^2 \cdot \text{day}$, correspondingly. The timetable of leach rates dependence in **Figure 10** indicates that they

are close to residual rates, when solution becomes saturated and secondary minerals begin to form.

Such secondary minerals, which formed after 84 days, produced the continuous surface layer of secondary phases, which are shown in **Figure 11**.

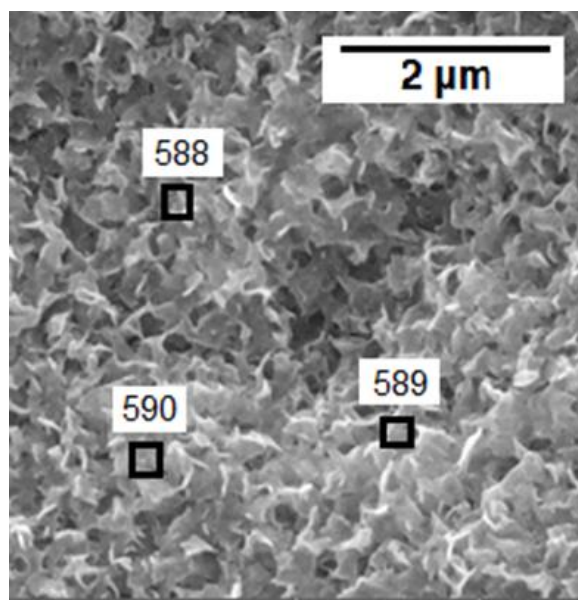


Figure 11: SEM observation of the surface after leach in deionized water for product 2 (pH=6.50, 84 days, 120 °C).

According to SED/EDS analysis (Table 5) the composition of this layer is practically the same and represents

alumosilicates of iron and nickel. Uranium and zirconium were not found in the surface layer.

Spectrum number	O	Al	Si	Fe	Ni	Total
588	66.13	15.17	12.01	3.22	3.48	100
589	66.26	15.19	11.74	3.56	3.24	100
590	64.07	16.26	12.21	3.80	3.66	100

Table 5: SEM/EDS analysis data of the continuous surface layer of secondary phases (at %).

Conclusion

The structure of completely melted at 2200-2500 °C simulated MCCI products represents silicate-based amorphous glassy-like phase where solid solutions of $(U_xZr_y)O_2$, iron-chromium spinel and cristobalite in form SiO_2 are distributed.

Leach behavior of MCCI products are practically the same in deionized and nitrated water with the most mass loss of calcium in acidic condition while of silicon and aluminum in alkaline media.

Leachates at 25, 50 and 90 °C after 28 and 56 days contained only Si, Ca, Al as a concrete's components. Uranium and zirconium in leachates were detected after 56 days at 120 °C. Normalized masses loss after 84 days were equal 10^{-5} and 10^{-6} g/cm² for zirconium and uranium correspondingly.

The secondary surface layers after leaching at 90 °C for 56 days were formed by compounds like $(Al_xFe_{1-x})O(OH)$, ferrous chlorite and opal $SiO_2 \cdot 2H_2O$.

Any secondary phases, containing uranium and zirconium, were not detected at all testing conditions.

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