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The Effect of Hydrogen Peroxide on a CST Under Cesium Ion Exchange Conditions

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ABSTRACT

About 10 years ago, a crystalline silicotitanate (CST) was synthesized using an alkali metal hydroxide and the alkoxides of titanium and silicon. TAM5 is a specific form of the developed CST. Later, TAM5 was modified by replacing about 25% of the titanium with niobium. The modified TAM5 was tested extensively to enable its use as an inorganic ion exchanger for the removal of radioisotopes, especially ^{137}Cs from highly alkaline nuclear waste solutions. IONSIV IE 911 is a granular form of modified TAM5 that is commercially available from UOP, LLC and was tested successfully at a pilot plant at Oak Ridge National Laboratory. In separate experiments, the degeneration of hydrogen peroxide was used to generate gas in situ to determine the effect of gas production on the column performance. These experiments led to experiments to determine the effect, if any, of hydrogen peroxide on the cesium partition coefficient (Cs K_d) and the CST structure. CST was equilibrated with alkaline

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nuclear waste simulants containing varying amounts of hydrogen peroxide (from trace to 1 M). The Cs loading on the CST was determined by atomic absorption (AA) spectroscopy. The dissolution of elements from CST to simulant was determined by inductively coupled argon plasma spectrometry. Powder X-ray diffraction spectrometry was used to determine the crystal structures in the CST. At trace levels, hydrogen peroxide does not have a significant effect on the Cs K_d or the CST structure. At higher concentrations (1 M or higher), the Cs Kd drops and the tetragonal phase, the major component of the CST, slowly dissolves into the simulant. Furthermore, the XRD pattern changes, indicating the dissolution of the tetragonal crystal structure, which is the phase in TAM5 that is selective for cesium.

INTRODUCTION

In 1990, a new crystalline silicotitanate, (TAM5) was synthesized by hydrothermal synthesis using sodium hydroxide and the alkoxides of titanium and silicon.[1,2] The crystalline structure of TAM5 is similar to that of sitinakite, a rare Russian mineral with the pharmacosiderite structure.[3,4] The structures of sitikanite and pharmacosiderite are well established. TAM5 has straight uniform channels of approximately 3.5 Å diameter, and belongs to a new class of materials similar to zeolites. Typical crystal sizes are in the range of 0.1 to 0.4 μm. Sodium ions are ion exchangeable with protons and also with other alkali metal ions without affecting the crystal structure. Since the channel size of TAM5 and the diameter of Cs ions are very close, ion exchange with Cs ions is almost irreversible.[5]

Replacing about 25% of the titanium atoms with niobium atoms modifies TAM5. The resulting product was tested extensively to enable its use as an inorganic ion exchanger for the removal of radioisotopes, especially ^{137}Cs, from highly alkaline nuclear waste solutions. IONSIV IE-911 is a granular form of modified TAM5 that is commercially available from UOP, LLC. During the last decade, we acquired unique expertise in the synthesis of crystalline silicotitanates (CST). We also synthesized silicotitanates from inorganic precursors in aqueous solutions without the use of any organics, such as alkoxides and chelates. Additionally, alternative alkali metal hydroxides can replace the use of sodium hydroxide. By using other alkali metal ions, different products are produced. The alkali metal ion used controls the channel diameter, as well as whether the channel network is parallel, as in TAM5, or intercepting at right angles, as in TAM4.

The current version of granular crystalline silicotitanate (TAM5) is commercially available from UOP, LLC under the trade name IONSIV

IE-911. TAM5 was extensively tested by several researchers and was determined as the best currently available material for removing cesium from various types of nuclear wastes salt solutions stored at various DOE sites. The studies at Savannah River Technology Center (SRTC) indicated that the IONSIV IE 911 granules tend to leach into the nuclear waste simulants during the operation of the ion-exchange columns. The production of gases by radiolysis was speculated to have an effect on the selective ion exchange of cesium. Hydrogen peroxide was used in testing at ORNL to generated gas to determine the effect of gas production on column operation. These experiments raised the question of a possible effect of hydrogen peroxide on the selective removal of cesium using the CST.

Silicotitanate Crystal Structure

Extensive search by J. Krumhansl of Sandia National Laboratory revealed that TAM5 is structurally related to a rare Russian mineral, sitinakite, from

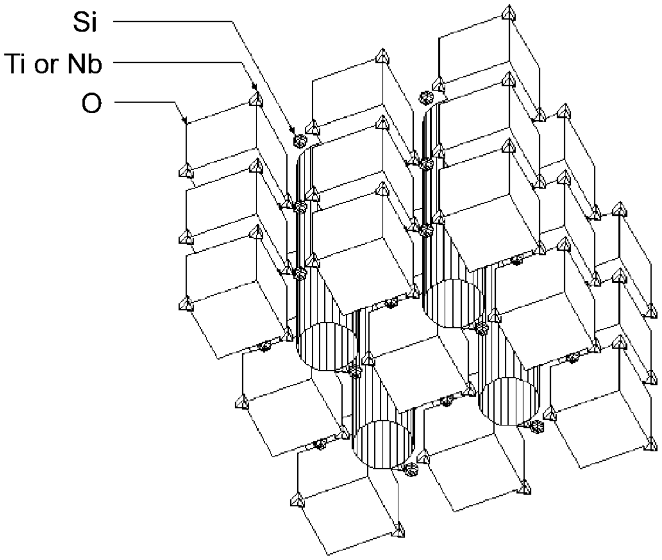

Figure 1. The TAM5 structure is illustrating the parallel channels. Each cube encloses a Ti_3NbO_4 cluster. Na is between a pair of Si, where Na is not shown. —Na—O—Si—O— strings are parallel to the channels.

Kibinskii alkaline massif. The idealized formula for the mineral is $Na_2(H_2O)_2Ti_4O_5(OH)(SiO_4)_2K(H_2O)_{1.7}$. Similarly, the formula for TAM5 is $Na_2(H_2O)_2Ti_4O_5(OH)(SiO_4)_2Na(H_2O)_{1.7}$. The presence of potassium is the major distinction between sitinakite and TAM5. The sitinakite also contains about 5 wt% of niobium, as well as small amounts of other elements.

The crystal structure of sitinakite was established by the single crystal XRD work by Sokolova et al.[4] They pictured that the crystal consists of (1) a column built with clusters of four octahedral Ti atoms linked with oxygen and (2) a string of alternating Si tetrahedra and Na octahedra. When four columns are attached with four strings, a straight channel of 3.5 A is created, where the columns and strands are parallel to each other.[4] Potassium ions and water molecules occupy the channels in sitinakite. Sodium ions and water molecules occupy the channels in TAM5. A drawing of TAM5 emphasizing the channels is shown in Fig. 1. In the XY projection, cubes are bridged with silicate groups to form the TAM5 structure. Within the cubes, Ti and O occupy alternate corners. In the *z*-axis direction, silicate groups are linked by sodium ions to

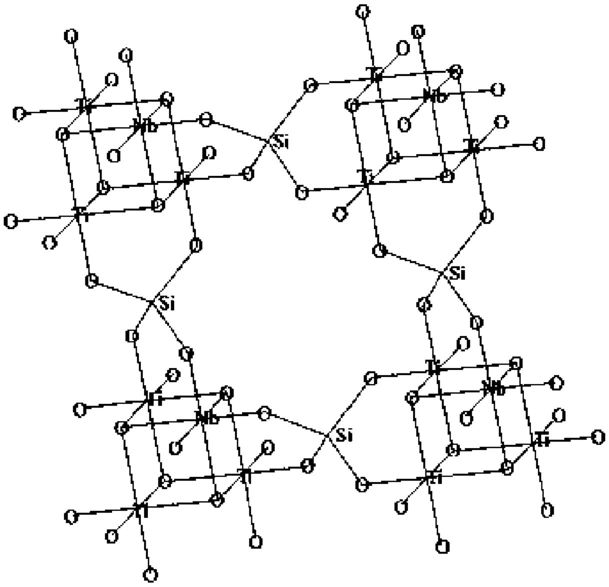

Figure 2. A section of TAM5 structure showing the Ti_3Nb clusters linked with tetrahedral silicates. The cross-section of a channel illustrated in Fig. 1 is the hole in the center with eight oxygen atoms, which can chelate with a cesium ion or other alkali metal ion.

form a straight (—O—Si—O—Na—)$_n$ strand. In TAM5, the cubes are linked by oxygen in the *z*-axis direction. TAM5 has parallel channels (3.5 A diameter) perpendicular to the XY projection. The molecular structure of the Ti_4 cluster bridges by silicate groups and the channel are illustrated in Fig. 2.

During the hydrothermal synthesis, high alkalinity with sodium hydroxide is extremely critical for the formation of the TAM5 structure.

The alkali hydroxide plays a template role during the synthesis of TAM5. Once the crystals are synthesized, the alkali metal ions are easily ion exchanged with protons using a strong acid, e.g., 2-M HCl, while keeping the crystal structure intact.[5] H-form TAM5 can be loaded with other alkali metal ions, which are larger than a Na ion. Larger ions can only occupy the channels.

The performance of a CST as an ion exchanger is very difficult to predict. The TEM of CST indicates a major phase with high crystallinity that is structurally similar to sitinakite, a second phase rich in silicate, and a third phase of mostly of niobate. The powder XRD patterns of CST and elemental compositions of CST with good Cs loading capacity are similar.

Evaluation of TAM5 Using Cs Distribution Coefficient (K_d) Experiments

The ion-exchange capacity of a CST was initially used to determine the quality of the material from each synthesis batch. For that purpose, a standard nuclear waste simulant (5.1-M $NaNO_3$, 0.6-M NaOH, 100-ppm Cs) was created. Generally, 100 mg of CST and 10 mL of standard simulant were transferred to a plastic vial, closed, and then shaken continuously for 48 hours using Burrel Wrist-Action shaker. The vial was then centrifuged, using an IEC EXD Centrifuge (Damion/IEC Division), at 60% power for 10 minutes. The clear supernatant liquid was separated from the vial, and then the Cs levels in the supernatant liquid and a control (basic salt solution without the CST shaken for 48 hours) were determined using a Varian AA 30 atomic absorption spectrometer. The Cs distribution coefficient (K_d) was calculated[a] and the quality of TAM5 was determined using the K_d. The amount of Ti, Si, and Nb in the supernatant liquid was determined by elemental analysis using an inductively coupled argon plasma spectrometer (ICAP, Thermo Jarrel Ash Model Poly Scan 61E). The very low level of Ti, barely above the background, indicated that no TAM5 was present in the supernatant liquid. Membrane filters with 0.2-micron pores were also tested to separate the CST from the supernatant liquid; it was observed that centrifuging was as effective as

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[a] Kd = g of Cs in g of solid phase (CST)/g of Cs in mL of liquid phase (simulant).

Table 1. Simulant 1 (basic salt solution, with 0.16-M Na_2CO_3).

Concentration	Weight/L
4.78-M $NaNO_3$	406 g of $NaNO_3$
0.6-M NaOH	48.02 g of NaOH (wt 50%)
0.16-M Na_2CO_3	16.96 g of Na_2CO_3
100-ppm Cs	0.1271 g of CsCl

filtration using membrane filters. Si and Nb were typically found at high levels. The source of Si and Nb could be from phases other than TAM5 crystals.

Ion-Exchange Experiments for a Performance Evaluation—A Comparative Study of CST Samples from Four Different Batches

IONSIV IE-910 (crystalline form) from UOP, LLC (UOP), TAM5 prepared by Ding Gu (DG141), and TAM5 (TAM5-4 and TAM5-5) are the four CST samples used in the study. UOP and DG141 were 6-year-old samples. Both TAM5-4 and TAM5-5 were synthesized in June 2000. The samples were heated at 400°C overnight and weight losses were determined.

Table 2. Average cesium distribution coefficients (K_d) in Simulant 1 (basic salt solution, with 0.16-M Na_2CO_3).

Name	1 day	2 days	5 days
UOP	850	983	1080
DG141	1066	1141	1143
TAM5-4	1085	1122	1212
TAM5-5	1053	1121	1149

After 2 days, there is very little change in the distribution coefficients for DG141 and TAM5-5. If one compares the distribution coefficients for TAM5-4, TAM 5-5, and DG 141, the differences are well within the standard deviations. These three batches were prepared using the same procedures. The UOP samples have lower values for the distribution coefficients; this is probably due to the synthesis of UOP samplesat lower temperatures than samples.

Table 3. Leaching of Si, Ti, and Nb from CST as a result of shaking with simulant 1.

Name	SiO_2 wt%	TiO_2 wt%	Nb_2O_5 wt%	Na_2O	Wt% dissolved
1-day					
UOP	0.31	0.03	0.12	0.10	0.55
DG141	0.17	0.01	0.06	0.05	0.28
TAM5-4	0.63	0.02	0.20	0.19	1.04
TAM5-5	0.65	0.01	0.10	0.18	0.94
2-day					
UOP	0.38	0.03	0.14	0.12	0.67
DG141	0.22	0.01	0.09	0.07	0.38
TAM5-4	0.71	0.02	0.23	0.21	1.17
TAM5-5	0.78	0.01	0.13	0.22	1.14
5-day					
UOP	0.40	0.03	0.15	0.12	0.70
DG141	0.29	0.02	0.15	0.10	0.55
TAM5-4	0.76	0.03	0.31	0.24	1.34
TAM5-5	0.81	0.01	0.14	0.23	1.20

The weight percentage of oxides of Si, Ti, and Nb that dissolved in the solution. This percentage is based on g of oxide of Si, Ti, or Nb per g of CST charged to the ion-exchange experiment times 100.

Since TAM5-4 and TAM5-5 were air-dried samples, they experienced 25% weight loss. They lost water and acetone during heating. The samples from UOP and from DG141 experienced 8% and 12% weight loss, respectively. All CST samples were composed of similar size crystals and used as received. Five simulants were prepared by varying the composition of our standard simulants by adding sodium carbonate and hydrogen peroxide. These studies were used to evaluate the effect of sodium carbonate and hydrogen peroxide

Table 4. Simulant 2 (basic salt solution with 0.0025-M H_2O_2, 0.16-M Na_2CO_3).

Concentration	Weight/L
0.0025-M H_2O_2	68.10 g of dil. H_2O_2
4.78-M $NaNO_3$	406 g of $NaNO_3$
0.6-M NaOH	48.02 g of NaOH (wt 50%)
0.16-M Na_2CO_3	16.96 g of Na_2CO_3
100-ppm Cs	0.1266 g of CsCl

Table 5. Average cesium distribution coefficients (K_d) and percentage relative standard deviations for Simulant 2 (0.0025-M H_2O_2, 0.16-M Na_2CO_3).

Name	1 day	2 days	6 days
UOP	1168	1051	1253
DG141	1153	1151	1287
TAM5-4	1203	1279	1447
TAM5-5	1134	1125	1322

on the K_d and the leaching of Si, Ti, and Nb from the CST during the equilibration experiments. The experiments were conducted in duplicates. K_d and leaching of Si, Ti, and Nb were determined as previously discussed.

ANALYSIS METHODS

Cesium was analyzed by atomic absorption using a Varian AA 30 atomic absorption spectrometer. The nuclear waste simulants were diluted 1:3 by

Table 6. Leaching of Si, Ti, and Nb from CST as a result of shaking with Simulant 2 (0.0025-M H_2O_2, 0.16-M Na_2CO_3).

Name	SiO_2 wt%	TiO_2 wt%	Nb_2O_5 wt%	Na_2O	Wt% dissolved
1-day					
UOP	0.33	0.03	0.12	0.10	0.58
DG141	0.22	0.01	0.08	0.07	0.37
TAM5-4	0.53	0.01	0.12	0.15	0.82
TAM5-5	0.59	0.01	0.08	0.16	0.84
2-day					
UOP	0.38	0.03	0.12	0.12	0.65
DG141	0.25	0.01	0.11	0.08	0.46
TAM5-4	0.61	0.02	0.18	0.18	0.98
TAM5-5	0.71	0.01	0.13	0.20	1.04
6-day					
UOP	0.42	0.03	0.15	0.13	0.74
DG141	0.29	0.02	0.15	0.10	0.56
TAM5-4	0.69	0.02	0.24	0.21	1.16
TAM5-5	0.76	0.01	0.16	0.22	1.15

Table 7. Simulant 3 (basic salt solution with 0.0025-M H_2O_2).

Concentration	Weight/L
0.0025-M H_2O_2	68.1 g of dil $2H_20_2$
4.78-M $NaNO_3$	406.29 g of $NaNO_3$
0.6-M NaOH	48.00 g of NaOH (wt 50%)
100-ppm Cs	0.1265 g of CsCl

adding water so that the capillary and the burner would not become clogged by the salt. The instrument was calibrated with cesium standard solutions and a blank with a similar matrix composition. The elemental analysis of Si, Ti, and Nb in the nuclear waste simulant samples was performed using an inductively coupled argon plasma (ICAP) spectrometer (Thermo Jarrel Ash Polyscan 61E). The simulants were diluted 1:3 by adding water to enhance the air sol formation. A Scintag XDS 2000 x-ray spectrometer was used to obtain the powder x-ray diffraction (XRD) pattern of solid samples. After equilibration with nuclear simulants, the CST solids were separated by a centrifuge, washed with water and acetone, air-dried, and scanned for the XRD patterns. A 100-mg sample of CST was dissolved in 1 mL 50% HF, water was added to make a 10 mL solution, and it was further diluted as needed for the ICAP.

Five simulants were prepared by adding sodium carbonate and hydrogen peroxide into the standard nuclear simulant (5.1-M $NaNO_3$, 0.6-M NaOH, 100-ppm Cs). The compositions of five simulants are listed in the Tables 1–13 for Simulants 1 to 5. Potassium permanganate titration was used to estimate hydrogen peroxide in the simulant before and after ion-exchange experiments. Initial hydrogen peroxide concentration in Simulant 2 was 0.0025 M. Simulant 4 and Simulant 5 had hydrogen peroxide concentrations of 0.1 M and 1 M. Hydrogen peroxide in the simulant decomposed continuously and the presence

Table 8. Average cesium distribution coefficient (K_d) and percentage relative standard deviations for Simulant 3 (0.0025-M H_2O_2).

Name	1 day	2 days	5 days
UOP	969	990	961
DG141	1209	1110	1077
TAM5-4	883	1191	1162
TAM5-5	980	1205	1181

Table 9. Leaching of Si, Ti, and Nb from CST as a result of shaking with Simulant 3 (0.0025-M H_2O_2).

Name	SiO_2 wt%	TiO_2 wt%	Nb_2O_5 wt%	Na_2O	Wt% dissolved
1-day					
UOP	0.33	0.04	0.14	0.11	0.62
DG141	0.27	0.01	0.07	0.08	0.43
TAM5-4	0.71	0.01	0.11	0.20	1.04
TAM5-5	0.73	0.01	0.06	0.20	0.99
2-day					
UOP	0.41	0.04	0.16	0.13	0.73
DG141	0.32	0.01	0.10	0.10	0.53
TAM5-4	0.79	0.02	0.16	0.23	1.19
TAM5-5	0.83	0.01	0.08	0.23	1.14
5-day					
UOP	0.51	0.04	0.18	0.16	0.89
DG141	0.35	0.02	0.14	0.11	0.62
TAM5-4	0.90	0.03	0.24	0.26	1.43
TAM5-5	0.96	0.01	0.12	0.26	1.36

of CST did not have any significant effect on the rate of decomposition of H_2O_2 to H_2O and O_2. In 9 days, H_2O_2 concentrations dropped from 1 M to about 0.1 M.

We did not conduct any experiments specifically to monitor the catalytic effect of CST on H_2O_2 decomposition. We conducted three series of experiments involving 1-day, 2-day, and 5-day continuous shaking for estimating the K_d values of CST samples along with the controls (simulant with out CST). The 2-day experiments did not show any catalytic activity by the CST. The 1-day and 5-day experiments showed a slight trend toward decomposition of H_2O_2 by CST. Since CST did not show vigorous catalytic

Table 10. Simulant 4 (basic salt solution with 0.1-M H_2O_2).

Concentration	Weight/L
0.1-M H_2O_2	11.33 g of 30% H_2O_2
5.1-M $NaNO_3$	550.8 g of $NaNO_3$
0.6-M NaOH	48.00 g of NaOH (wt 50%)
100-ppm Cs	0.1265 g of CsCl

Table 11. Average cesium distribution coefficients (K_d) for Simulant 4 (0.1-M H_2O_2).

Name	1 day	2 days	5 days
UOP	1005	873	582
DG 141	833	627	520
TAM5-4	943	798	498
TAM5-5	963	757	524

activity, we concluded that CST by itself does not promote the decomposition of H_2O_2 significantly.

Determination of Hydrogen Peroxide by Titration with Potassium Permanganate

A stock solution of 0.1 M was prepared by dissolving 15.8 g of potassium permanganate in a volumetric flask and adding water to make of solution. This solution was diluted a -fold to obtain 0.001-M potassium permanganate.

Table 12. Leaching of Si, Ti, and Nb from CST as a result of shaking with Simulant 4 (0.1-M H_2O_2).

Name	SiO_2 wt%	TiO_2 wt%	Nb_2O_5 wt%	Na_2O	Wt% dissolved
1-day					
UOP	1.87	1.84	1.85	1.06	6.62
DG141	1.83	2.02	2.21	1.12	7.18
TAM5-4	1.68	1.56	2.08	0.98	6.30
TAM5-5	2.01	1.76	2.28	1.13	7.19
2-day					
UOP	3.76	4.70	3.79	2.32	14.57
DG141	5.91	5.32	5.97	3.25	20.46
TAM5-4	4.39	3.77	4.87	2.43	15.45
TAM5-5	5.05	3.82	5.22	2.65	16.75
5-day					
UOP	7.88	11.59	8.03	5.22	32.73
DG141	6.51	8.41	6.78	4.10	25.80
TAM5-4	8.41	11.59	10.31	5.62	35.93
TAM5-5	7.43	9.38	8.70	4.75	30.26

Table 13. Simulant 5 (basic salt solution with 1-M H_2O_2).

Concentration	Weight/L
1-M H_2O_2	113.3 g of 30% H_2O_2
5.1-M $NaNO_3$	550.8 g of $NaNO_3$
0.6-M NaOH	48.00 g of NaOH (wt 50%)
100-ppm Cs	0.1265 g of CsCl

Both solutions were used for the titration. Oxalic acid was used to standardize these solutions. The titration was performed by warming 1 mL of simulant and 10 mL of 2-M sulfuric acid in a 250 mL Erlenmeyer flask on a hot plate. Potassium permanganate solution was added from a 50-mL burette. Since the reaction between hydrogen peroxide and potassium permanganate is slow at room temperature, during the titration the temperature of the solution was maintained at 65 to 85°C. A pink color lasting longer than 30 seconds indicated the end point.

RESULTS AND DISCUSSION

In this work, the simulants were separated from the solids by a centrifuge and analyzed by ICAP to estimate the leaching of Si, Ti, and Nb from CST during the equilibration experiments. Tables 3 through 15 and Figs. 3 to 6 show the analysis results. The elemental analysis of the first three simulants does not show any significant amount of Ti loss, indicating that the CST phase with a sitinakite structure is very stable. Leaching of a small amount of

Table 14. Average cesium distribution coefficients (K_d) for simulant 5 (1-M H_2O_2).

Name	1 day	2 days	5 days
UOP	783	437	204
DG	615	412	120
TAM5-4	687	283	78
TAM5-5	570	163	43

Table 15. Leaching of Si, Ti, and Nb from CST as a result of shaking with Simulant 7 (1-M H_2O_2).

Name	SiO_2 wt%	TiO_2 wt%	Nb_2O_5 wt%	Na_2O	Wt% dissolved
1-day					
UOP	6.66	8.15	7.20	4.14	26.14
DG141	8.43	8.06	8.70	4.75	29.94
TAM5-4	8.05	5.10	8.36	4.04	25.55
TAM5-5	9.15	5.91	9.28	4.59	28.93
2-day					
UOP	7.34	7.86	6.73	4.20	26.14
DG141	12.96	8.41	11.06	6.27	38.69
TAM5-4	12.70	8.61	11.89	6.34	39.54
TAM5-5	14.62	6.49	11.55	6.38	39.04
5-day					
UOP	15.13	24.60	17.38	10.70	67.82
DG141	16.21	27.13	20.70	11.86	75.90
TAM5-4	14.33	23.55	19.80	10.58	68.26
TAM5-5	15.36	22.02	19.14	10.47	66.98

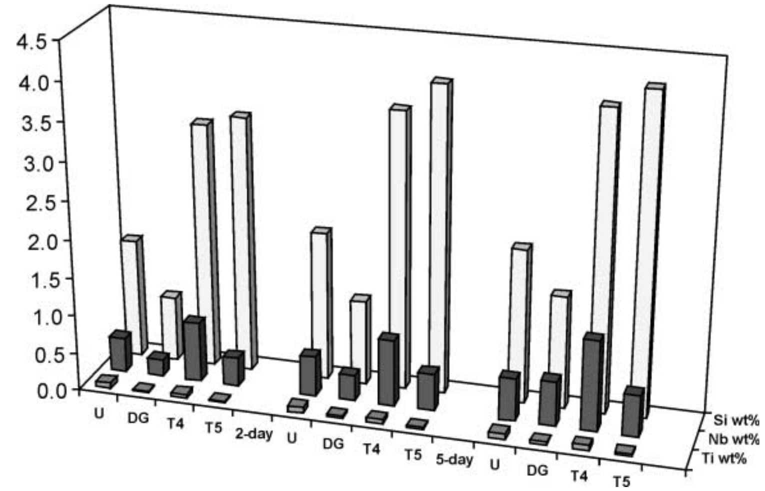

Figure 3. Leaching of Si, Ti, and Nb from CST as a result of shaking with simulant #1 (basic salt solution with 0.16-M Na_2CO_3).

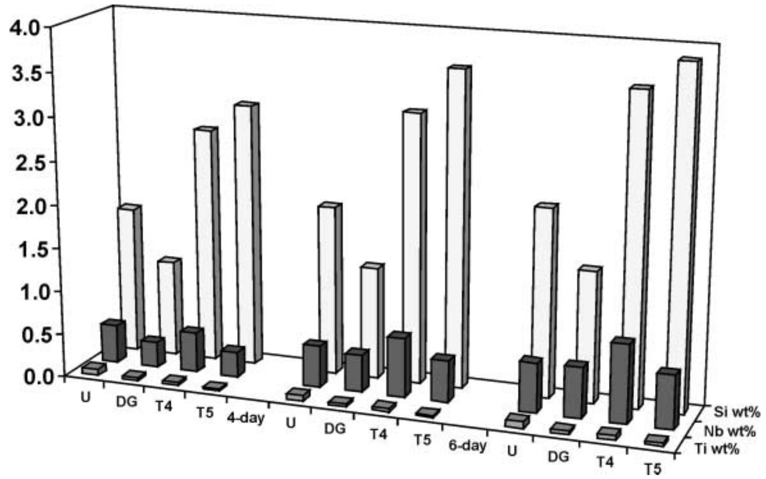

Figure 4. Leaching of Si, Ti, and Nb from CST as a result of shaking with simulant #2 (basic salt solution with 0.16-M Na_2CO_3 and 0.0025 M H_2O_2).

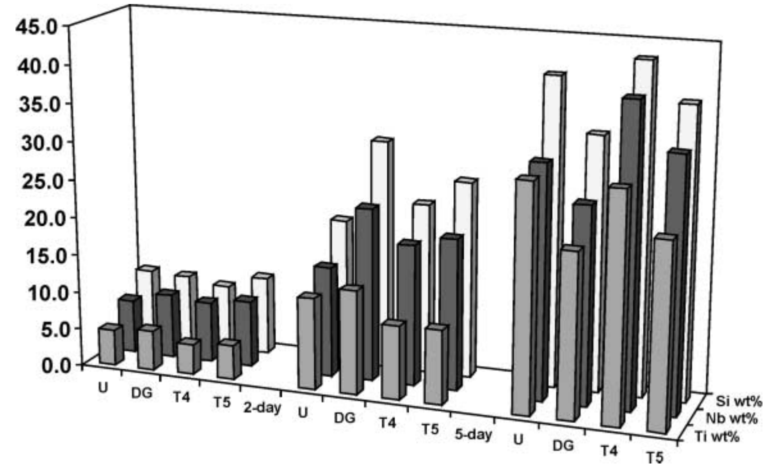

Figure 5. Leaching of Si, Ti, and Nb from CST as a result of shaking with simulant #4 (basic salt solution with 0.1-M H_2O_2).

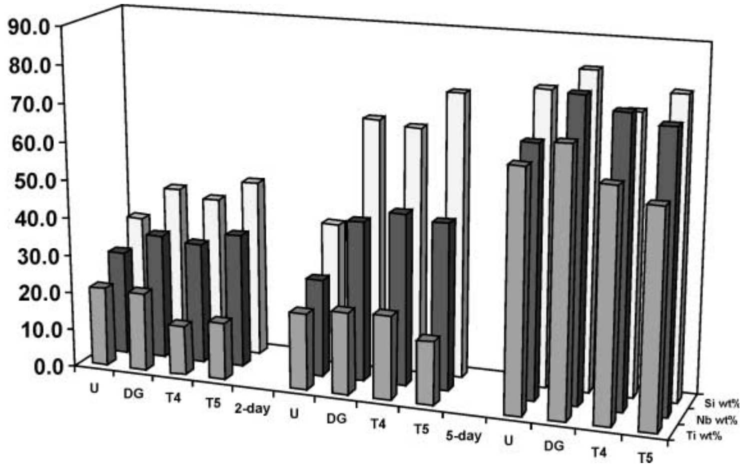

Figure 6. Leaching of Si, Ti, and Nb from CST as a result of shaking with simulant #4 2 (basic salt solution with 1-M H_2O_2).

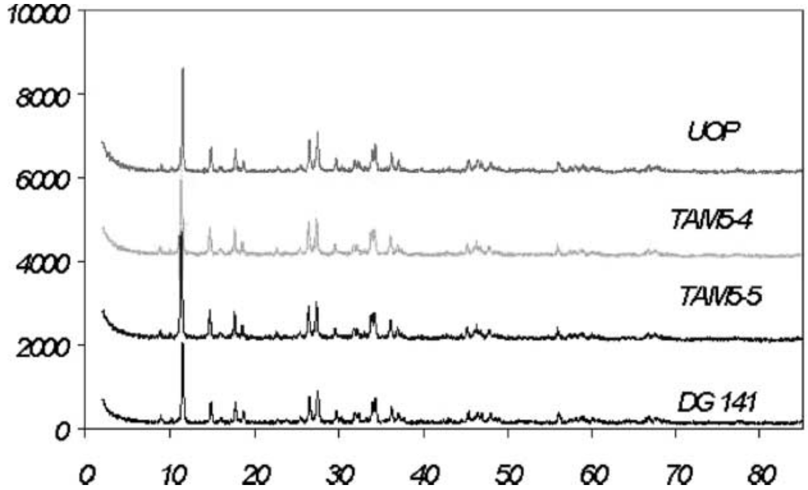

Figure 7. XRD pattern of CSTs before shaking with basic simulants.

Table 16. XRD peaks of two phases separated by the aid of hydrogen peroxide treatment (Figs. 5 and 10).

Tetragonal phase		Nb/Ti oxide phase	
2-theta	CPS	2-theta	CPS
14.6	839	9.1	1281
15.9	326	10.0	668
17.5	839	11.2	766
18.4	500	14.6	430
22.6	317	15.7	656
25.3	434	17.6	458
26.4	961	19.6	309
27.4	1030	22.6	240
31.8	413	23.6	396
33.7	735	25.3	598
34.2	778	26.6	743
36.2	613	27.6	523
37.1	430	29.7	1795
39.6	230	30.2	546
42.6	265	32.1	401
45.1	439	34.2	454
46.3	508	35.8	442
47.8	369	39.6	401
55.6	439	45.1	280
57.7	274	48.2	332
58.7	308	51.4	401
60.0	300	55.8	274
60.8	247	58.1	309
66.7	308	60.4	390
67.4	291	66.5	222
74.3	195		
77.0	195		

the silicate and niobate phases is indicated by the presence of dissolved Si and Nb species in the simulant. About one third of the CST broke down in Simulant 4 with 0.1-M H_2O_2 and over two-thirds of the CST broke down in Simulant 5 with 1-M H_2O_2 over a 5-day period.

When samples of CST were equilibrated with Simulant 1 and 2, containing carbonates, Cs K_d values (see Tables 2 and 5) increased with

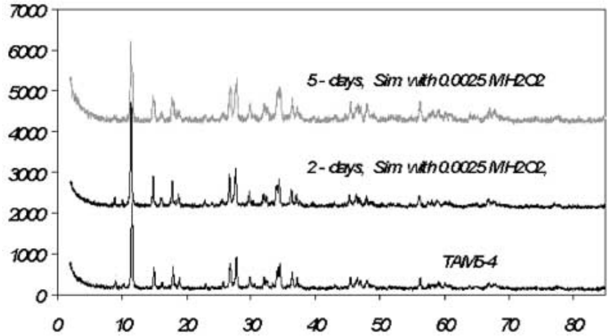

Figure 8. Effect on the XRD pattern of CST as a result of shaking with basic simulant containing 0.0025-M H_2O_2.

equilibration time. It appears that the presence of 0.0025 M H_2O_2 does not have any effect on the Cs K_d values. Simulant 3 contained 0.0025 M H_2O_2 but no carbonates. Table 8 shows that in simulant 3, Cs K_d values decreased with increased equilibration time, from 2 days to 5 days. Generally, Cs K_d values increased with longer equilibration time. At least in simulants with low concentrations of hydrogen peroxide, carbonate apparently inhibits the effect of hydrogen peroxide. Carbonate is structurally similar to silicate and titanate and has the ability to inhibit their dissolution from the CST. Thus, carbonate is

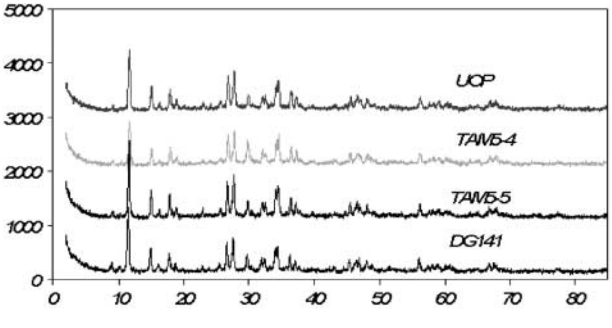

Figure 9. Effect on the XRD pattern of CST as a result of shaking with basic simulant containing 0.1-M H_2O_2 for 2 days.

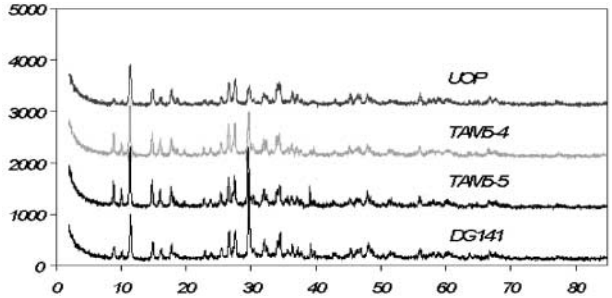

Figure 10. Effect on the XRD pattern of CST as a result of shaking with basic simulant containing 1-M H_2O_2 for 2 days.

a stabilizing agent for the CST. Tables 11 and 14 show the effect of hydrogen peroxide at 0.1- and 1-M concentrations on Cs K_d values over 5 days of equilibration. At the end of 5 days of equilibration, a 40% decrease of Cs K_d was observed in simulant 4. In Simulant 5, which contained 1-M hydrogen peroxide, the Cs K_d values dropped as much as 95%. The weight percentage of CST dissolved in the five simulants are listed in Tables 3 through 13. In 5 days, about 1 wt % of CST dissolved in simulants 1and 2 while slightly more dissolved in simulant 3. In simulant 4 with 0.1-M H_2O_2, as much as 35 wt% of CST dissolved in 5 days. As much as 75% of CST dissolved in simulant 5 with

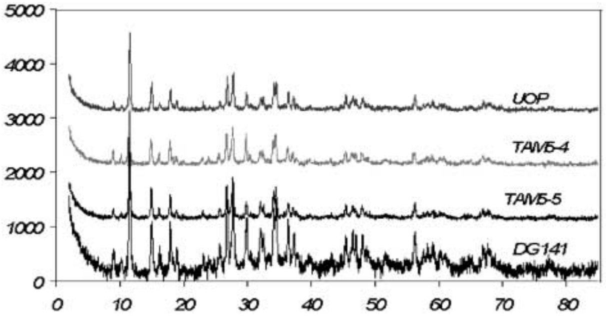

Figure 11. Effect on the XRD pattern of CST as a result of shaking with basic simulant containing 0.1-M H_2O_2 for 5 days.

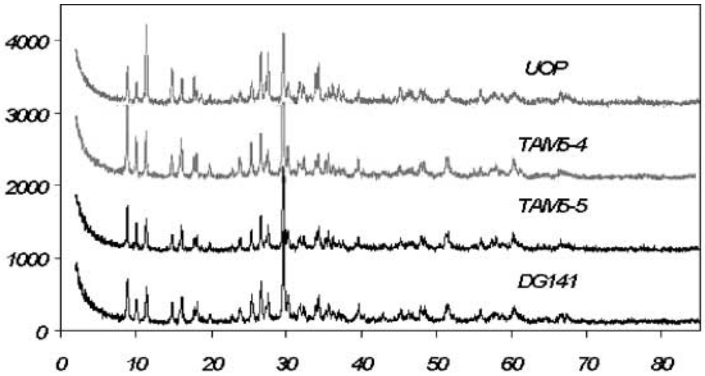

Figure 12. Effect on the XRD pattern of CST as a result of shaking with basic simulant containing 1-M H_2O_2 for 5 days.

1-M H_2O_2 after 5 days equilibration. The lowering of Cs K_d parallels the dissolution of CST in the simulants. However, overall percentage decreases in Cs K_d outpaced wt% dissolution of CST. There are three phases that exist in a typical sample of CST. Only a tetragonal phase, which accounts for at least 90% of the CST, is known to have high Cs ion-exchange capacity. This is the first indication that hydrogen peroxide causes the selective dissolution of the tetragonal phase in basic simulants. Figures 3 through 6 illustrate the dissolution in wt% of each element oxide from the CST into simulants 1,2,3,4, and 5. After 5 days of equilibration in Simulant 5, the same wt% of each element oxide dissolved from CST. Hydrogen peroxide attacks the tetragonal phases and solubilizes its components. As a result, the CST structure as well as the ion-exchange capacity, is lost.

The XRD patterns of four samples of CST are shown in Fig. 7. All of the major peaks, which are also listed in Table 16, belong to the tetragonal phase. Four minor peaks (2 theta = 9, 10, 15.9, 29.7) belong to the minor phase (Nb/Ti oxide). Figures 8 through 12 show the XRD pattern of CST samples exposed to simulants with hydrogen peroxide. Hydrogen peroxide attacks the tetragonal phase and the intensity of XRD peaks changes proportionally to the exposure time, as well as the concentration of hydrogen peroxide. The intensity of XRD pattern of the tetragonal phase decreases, while that of the minor phase increases. The XRD patterns shown in Fig. 10 indicate that after 5 days of exposure to simulant with 1 M hydrogen peroxide, most of the tetragonal phase in

Table 17. Effect of treatment with simulant containing 1-M hydrogen peroxide.

CST-exposure (days)	Nb/Ti
UOP-1	0.38
UOP-2	0.45
UOP-5	0.60
DCG-1	0.46
DG-2	0.56
DG-5	0.96
TAM5-4-1	0.46
TAM5-4-2	0.59
TAM5-4-5	1.12
TAM5-5-1	0.38
TAM5-5-2	0.51
TAM5-5-5	0.83

the CST samples disappeared and Nb/Ti ratio of the solid increases from 0.4 to 1 (Table. 17). TEM has identified the minor phase in the CST as Nb-Ti oxide phase with a Nb/Ti ratio close to 2.

CONCLUSION

Carbonate may prevent the degradation CST by hydrogen peroxide, which is a product of radiation. A careful examination of data reveals that hydrogen peroxide, even at very low concentration, has a degrading effect on CST.

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