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CANDIDATE GLASS-CERAMIC WASTE FORMS FOR IMMOBILIZATION OF THE CALCINES STORED AT THE IDAHO CHEMICAL PROCESSING PLANT

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ABSTRACT

Candidate glass-ceramic waste forms for immobilization of the major types of calcines stored at the Idaho Chemical Processing Plant (ICPP) were synthesized and characterized. The waste forms were prepared by hot isostatically pressing a mixture 70 wt% of precompacted simulated non-radioactive calcine and 30 wt% additives (Silica and Al or Ti metal powders). The types of calcines stored in stainless steel Bin Sets at the ICPP are fluorinel/sodium (F/Na), alumina, zirconia, zirconia/sodium (Zr/Na), and zirconia-alumina (Zr-Al). In addition to the silica additive, glass-ceramics for F/Na and alumina calcines were prepared and characterized using ICPP soil and clay additives. The characteristics of the waste forms including density, elastic properties, chemical durability, glass and crystalline phases, phases separation, and the microstructure were investigated. The 28-day MCC-1 test for chemical durability was used for all the waste forms. In addition, the Product Consistency Test (PCT) was conducted for the glass-ceramics, and the normalized elemental releases in g/m^2 were compared with the Environmental Assessment (EA) glass. The characteristics of the soil and clay glass-ceramics appear to be as good as the waste forms prepared with silica. The glass-ceramic waste forms recommended are: 5Ti-Clay, or 5Ti-Soil, or 5Ti-Silica for the fluorinel/sodium calcine; clay or silica for the alumina calcine; and 5Ti-Silica for the zirconia, Zr/Na, and Zr-Al calcines. Soil- and clay-based glass-ceramics offer an opportunity to incorporate contaminated waste into durable low volume waste forms.

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INTRODUCTION

Since early the 80s, durable glass-ceramics have been developed and characterized at the Idaho Chemical Processing Plant (ICPP). Glass-ceramics appear to be suitable waste forms for immobilization of the high level solid wastes, Fluorinel/sodium (Fl/Na), alumina, zirconia, zirconia/sodium (Zr/Na), and zirconia-alumina (Zr-Al) calcines that are stored in stainless steel Bin Sets at the ICPP. Candidate glass-ceramic waste forms were synthesized at ICPP by hot isostatically pressing a mixture of precompacted non-radioactive simulated calcine and additives at 1050 °C, 20,000 psi for 4 hours.¹⁻³ The calcine and the additive contents for the candidate waste forms for immobilization of the Fl/Na, alumina, zirconia, Zr/Na, and Zr-Al calcines are given in Table I. The calcine waste loading was 70 wt%. Additives include silica, soil, clay, aluminum metal powder, titanium metal powder, Na₂O, B₂O₃, and Li₂O. In addition to the silica additive, glass-ceramics for Fl/Na and alumina calcines were prepared using ICPP soil and clay additives. The composition of the ICPP soil is given in Reference 5. The composition of clay is 73 wt% SiO₂, 16.2 wt% Al₂O₃, 3.9 wt% Fe₂O₃, 2.7 wt% Na₂O, 2.2 wt% MgO, 1.2 wt% K₂O, 0.6 wt% TiO₂, and 0.2 wt% CaO. Chemical composition of calcines (except for zirconia calcine), formulations for glass-ceramic waste forms, and experimental procedures are discussed elsewhere.³⁻⁵ In this paper, the candidate glass-ceramic waste forms for immobilization of the major types of calcines stored at the ICPP, the characteristics including density, elastic properties, chemical durability, glass and crystalline phases, phases separation, and the microstructure are discussed.

Table I. Calcine and Additive Composition (wt%)

Waste Form	Calcine Type & Loading	Silica	Soil	Clay	Al	Ti	Na ₂ O	B ₂ O ₃	Li ₂ O
Fl/Na 2Al-Silica	Fl/Na 70.0	28.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0
Fl/Na 2Al-Soil	Fl/Na 70.0	0.0	28.0	0.0	2.0	0.0	0.0	0.0	0.0
Fl/Na 2Al-Clay	Fl/Na 70.0	0.0	0.0	28.0	2.0	0.0	0.0	0.0	0.0
Fl/Na 5Ti-Silica	Fl/Na 70.0	23.9	0.0	0.0	0.0	5.0	0.0	1.1	0.0
Fl/Na 5Ti-Soil	Fl/Na 70.0	0.0	23.9	0.0	0.0	5.0	0.0	1.1	0.0
Fl/Na 5Ti-Clay	Fl/Na 70.0	0.0	0.0	23.9	0.0	5.0	0.0	1.1	0.0
Alumina Silica	Alumina 70.0	30.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Alumina Soil	Alumina 70.0	0.0	30.0	0.0	0.0	0.0	0.0	0.0	0.0
Alumina Clay	Alumina 70.0	0.0	0.0	30.0	0.0	0.0	0.0	0.0	0.0
Zirconia 5Ti-Silica	Zirconia 70.0	20.2	0.0	0.0	0.0	5.0	2.2	1.8	0.8
Zr/Na 5Ti-Silica	Zr/Na 70.0	21.8	0.0	0.0	0.0	5.0	1.6	1.6	0.0
Zr-Al 5Ti-Silica	Zr/Al 70.0	20.1	0.0	0.0	0.0	5.0	2.3	1.8	0.8

* Zirconia and alumina calcines in Bin Set II.

RESULTS, DISCUSSION, AND CONCLUSIONS

The nominal chemical compositions of the waste forms and Young's modulus are given in Table II. Silica ranges between 16 wt% for the Fl/Na 5Ti-Soil waste form and 30 wt% for the

Table II. Nominal Composition of the Waste Forms in wt% And the Young's Modulus in GPa.

Waste Form	FI/Na 2Al- Silica	FI/Na 2Al- Soil	FI/Na 2Al- Clay	FI/Na 5Ti- Silica	FI/Na 5Ti- Soil	FI/Na 5Ti- Clay	Alumina Silica	Alumina Soil	Alumina Clay	Zirconia- 5Ti- Silica	Zr/Na 5Ti- Silica	Zr-Al 5Ti- Silica
Al ₂ O ₃	8.4	12.3	13.9	5.7	9.0	9.6	64.1	68.2	68.9	10.0	12.6	24.4
B ₂ O ₃	3.1	3.1	3.0	4.1	3.0	3.0	0.4	0.4	0.4	1.9	1.8	2.5
CaF ₂	24.4	24.4	24.2	23.9	23.8	23.8	1.2	1.2	1.2	23.7	26.4	17.6
CaO	8.0	9.8	7.9	7.8	9.3	7.8	0.4	2.3	0.5	18.0	12.0	13.2
CdO	2.8	2.8	2.7	2.7	2.7	2.7	0.0	0.0	0.0	0.03	0.03	0.07
CeO ₂	0.7	0.7	0.7	0.7	0.7	0.7	0.0	0.0	0.0	0.07	0.01	0.07
Cr ₂ O ₃	0.8	0.8	0.8	0.8	0.8	0.8	0.1	0.1	0.1	0.5	0.5	0.4
Cs ₂ O	0.1	0.1	0.1	0.1	0.1	0.1	0.4	0.4	0.4	0.2	0.07	0.3
Fe ₂ O ₃	0.2	1.6	1.3	0.2	1.4	1.1	0.4	1.9	1.6	0.1	0.07	0.2
K ₂ O	1.2	1.5	1.5	1.1	1.4	1.4	0.1	0.5	0.5	0.0	0.6	0.1
MgO	0.0	1.0	0.6	0.5	1.3	0.5	0.0	1.6	0.7	0.0	0.0	0.0
Na ₂ O	3.7	4.2	4.4	3.6	4.0	4.2	1.8	2.3	2.6	2.4	4.0	2.4
SiO ₂	27.8	18.4	20.1	23.2	16.0	17.7	30.0	19.9	21.9	20.1	21.6	20.1
SrO	0.4	0.4	0.4	0.4	0.4	0.4	0.0	0.5	0.5	0.6	0.1	0.6
TiO ₂	0.0	0.2	0.2	7.8	8.2	8.2	0.0	0.2	0.2	5.8	5.8	5.8
ZrO ₂	11.7	11.7	11.6	11.5	11.4	11.4	0.6	0.6	0.6	15.8	13.9	11.7
Misc.	6.5	6.8	6.4	6.3	6.3	6.3	0.0	0.0	0.0	0.0	0.7	0.0
Young's modulus	64.8	75.8	75.8	78.6	84.8	77.2	101.0			82.1	68.3	

alumina waste form. Iron and magnesium contents were high in the clay and soil waste forms compared to the waste forms prepared with silica. The Young's modulus of these waste forms ranged between 65 and 101 GPa (9.4 and 14.6 million psi). The Young's moduli of the FI/Na-Soil waste forms are higher, and thus stronger than the FI/Na-Silica waste forms. The Young's modulus for the alumina-silica is the highest at 101 GPa (14.6 million psi). The Young's modulus is related to the strength and the thermal expansion coefficient of the material. Higher the Young's modulus, higher the material strength, and lower the thermal expansion coefficient. The densities of the waste forms for FI/Na, alumina, zirconia, Zr/Na, and Zr/Al calcines are 3.2, 3.0, 3.1, 2.9, and 3.1 g/cm³, respectively.

The 28-day MCC-1 test⁶ for chemical durability was used for all the waste forms. In addition, the 7-day Product Consistency Test (PCT)⁷ was conducted for the glass-ceramics. The 28-day MCC-1 total mass loss rates (TMLRs) and the normalized elemental leach rates are presented in Table III. The TMLRs for these waste forms ranged between 0.01 and 0.20 g/m²-day. It appears that the TMLRs for the FI/Na waste forms are independent of the additives, silica, or soil, or clay, or Al, or Ti. For the soil and clay alumina waste forms, the TMLRs are significantly lower compared to the alumina-silica waste forms. The 28-day MCC-1 normalized elemental leach rates for aluminum, boron, calcium, cadmium, chromium, cesium, potassium, silicon, sodium, strontium, titanium, and zirconium are all less than 1 g/m²-day, except for the waste forms alumina-soil and Zr-Al 5Ti-Silica. For these two waste forms, the boron and the alkali leach rates are > 1 g/m²-day. The 7-day PCT was conducted for the crushed glass-ceramic powders of 100-200 mesh. The volume of the leachant solution (deionized water) was 40 mL per gram of the crushed glass-ceramic. The surface area to the volume ratio (SA/V) was about 444/m. The PCT normalized elemental releases in g/m² are compared with the Environmental Assessment (EA) glass⁸ in Table IV. The PCT normalized elemental releases for the glass-ceramics appear significantly lower than that of the EA glass. The SA/V for the EA glass was 2000/m. The 28-day MCC-1 and the 7-day PCT results provide information about the short term corrosion rate. There is a need to perform long term MCC-1 or PCT corrosion tests or the vapor hydration test for accelerated long term corrosion. However, it is cautioned that the changes in particle size distribution and the glass and crystalline phase distributions may impact the PCT estimates. If the releases are from the glass matrix only, then the SA/V is to be corrected for the fraction of the glass surface area given in Table III. The releases presented in Tables III and IV are for the glass-ceramic surface area rather than for the glass matrix only.

The XRD results are presented in Table V. The major crystalline phases for all the waste forms, except for the alumina waste forms, are calcium fluoride and zirconia. In addition for the FI/Na waste forms the crystalline phases include, cadmium sulphide, zircon, and titanates. The crystalline phases for the alumina waste forms are alpha, gamma, and delta alumina, cristobalite, albite, and mullite. The additional crystalline phases for the zirconia waste form are zirconolite, and zircon. For Zr/Na, the additional phases are Ca₂ZrTiO₆, and Ca₂SiO₄. The zircon crystals and the titanates (zirconolite, perovskite, and titanium oxides) have the capacity to host actinides, and the fission products, cesium and strontium, respectively.

The microstructure for the FI/Na waste form includes glassy regions that are devoid of macro crystalline grains; the alumina waste forms consist of rod like alumina crystals in a glassy matrix, and the zirconia waste form is similar to the FI/Na waste form. The crystalline phases, except nepheline (NaAlSiO₄), appear durable (see Table III for Na leach rates for Zr-Al). Glass phase separation was not detected in alumina and zirconia waste forms. In general, the glass and crystalline phases appear to be chemically durable, as the 28-day MCC-1 normalized elemental leach rates are less than 1 g/m²-day. The characteristics of the soil and clay glass-ceramics are as good as the waste forms prepared with silica.

The recommended candidate glass-ceramic waste forms for immobilization of the major types of calcines stored at the ICPP are: FI/Na 5Ti-(Clay, or Soil, or Silica), Alumina-Silica, or -Clay, Zirconia-5Ti-Silica, Zr/Na-5Ti-Silica, and Zr-Al-5Ti-Silica, respectively. The waste

Table III. The TMLRs, the Glass Surface Area Fraction, and the 28-day Normalized Elemental MCC-1 Leach Rates in g/m²-day.

Waste Form	TMLR ^a GlassArea ^a	Al ^b	B ^b	Ca ^b	Cd ^b	Cr ^b	Cs ^b	K ^b	Na ^b	Si ^b	Sr ^b	Ti ^b
FI/Na	0.13	0.26	0.08	0.15	0.10	0.03	0.00	0.17	0.20	0.36	0.30	^c
2Al-Silica	0.27											^c
FI/Na	0.16	0.28	0.11	0.14	0.04	0.07	0.13	0.58	0.46	0.15	0.61	^c
2Al-Soil	0.42											^c
FI/Na	0.15	0.22	0.04	0.13	0.04	0.06	0.00	0.31	0.22	0.13	0.41	^c
2Al-Clay	0.29											
FI/Na	0.15	0.22	0.08	0.14	0.03	0.03	0.31	0.32	0.77	0.27	0.32	0.00
5Ti-Silica	0.34											
FI/Na	0.17	0.28	0.08	0.13	0.04	0.07	0.15	0.48	0.39	0.17	0.45	0.02
5Ti-Soil	0.38											
FI/Na	0.17	0.26	0.07	0.14	0.03	0.07	0.13	0.47	0.51	0.17	0.43	0.02
5Ti-Clay	0.33											
Alumina Silica	0.08	0.01	0.36	^d	0.00	0.00	0.28	0.02	0.26	0.19	0.26	^c
Alumina Soil	0.02	0.04	9.63	0.01	0.00	0.00	1.01	1.18	3.49	0.21	0.00	0.00
Alumina Clay	0.01	0.01	0.37	0.37	0.00	0.00	0.20	0.34	0.17	0.09	0.21	0.01
Zirconia	0.20	0.43	0.62	^d	0.03	0.01	0.37	0.05	0.42	0.39	0.32	0.00
5Ti-Silica	0.30											
Zr/Na 5Ti-Silica	0.17 0.34	0.41	0.16	0.14	0.00	0.00	0.00	0.39	0.66	0.15	^d	0.02
Zr-Al ⁺ 5Ti-Silica	0.02	0.34	2.09	0.07	^d	0.00	1.39	0.46	1.21	^d	0.09	^d

a. Top number: TMLR: 28-day MCC-1 total mass loss rate, bottom number: glass matrix area fraction

b. 28-day MCC-1 normalized elemental leach rates

c.. No Ti in the waste

d. Not analyzed

e.. 27 wt% alumina calcine + 73 wt% zirconia calcine.

Table IV. Comparison of the 7-day PCT Normalized Elemental Releases in g/m² With EA Glass

Waste Form	Al	B	Ca	Cd	Cr	Cs	K	Na	Si	Sr	Ti
Fl/Na 2Al-Silica	0.17	0.23	0.11	0.00	0.01	0.05	1.90	1.34	0.10	0.00	
Fl/Na 2Al-Soil	0.21	0.33	0.26	0.00	0.00	1.03	0.65	0.64	0.08	0.00	
Fl/Na 2Al-Clay	0.13	0.24	0.14	0.01	0.00	0.05	0.31	0.38	0.09	0.00	
Fl/Na 5Ti-Silica	0.29	0.47	0.14	0.01	0.01	0.39	0.21	0.64	0.02	0.00	0.00
Fl/Na 5Ti-Soil	0.20	0.62	0.16	0.00	0.01	0.37	0.48	0.64	0.10	0.08	0.00
Fl/Na 5Ti-Clay	0.16	0.59	0.16	0.00	0.01	0.32	0.45	0.64	0.10	0.06	0.00
Alumina Silica	0.17	0.32	0.07	0.00	0.00	0.85	0.01	0.24	0.11	0.00	
Zirconia 5Ti-Silica	0.17	0.88	0.19	0.00	0.00	1.06	0.02	0.42	0.06	0.67	
EA Glass		4.54						3.58	1.04		

* Surface Area/Volume = 444 m² for the glass-ceramics, and 2000 m² for the EA glass
 If the releases are from glass matrix only, then the SA/V is to be corrected using the glass surface area fractions given in Table III.

Table V. XRD Results For The Waste Forms (Relative abundance in wt%)

Waste Form	CaF ₂	ZrO ₂	CdS	ZrSiO ₄	Ca ₂ (Al,Si) ₂ O ₇	NaAlSi ₃ O ₈	NaCaAlSi ₃ O ₇	Ca ₂ SiO ₄	CaZrTi ₂ O ₇	Cd	CaTiSiO ₅
Fl/Na 2Al-Silica	33.8	30.3		11.4	6.0	10.1					
Fl/Na 2Al-Soil	53.5	28.2	3.8			5.6	5.6	2.3			
Fl/Na 2Al-Clay	55.7	21.3	4.4								
Fl/Na: 5Ti-Silica	36.8	17.2		14.4						3.1	15.6
Fl/Na 5Ti-Soil	43.5	17.6	4.1						20.7	7.8	6.2
Fl/Na 5Ti-Clay	35.7	16.6	2.1						17.8	6.7	2.7
Zirconia 5Ti-Silica	32.5	19.2	5.6	3.9	Anorthite ^a 15.8	CaTiO ₃ 4.2	NaAlSi ₂ O ₆ 2.0			TiS 1.8	
Zr/Na 5Ti-Silica	54.7	24.3			Ca ₂ Zr ₂ Ti ₂ O ₆ 2.1	Ca ₂ SiO ₄ 3.1			3.3		12.5
Zr-Al 5Ti-Silica				Alpha Al ₂ O ₃ 3.9	CaAl ₂ Si ₂ O ₈ 21.6	NaAlSiO ₄ 8.6	CaTiO ₃ 2.4				
Alumina Silica	52.6	10.8		SiO ₂ 35.3	Alpha Alumina 35.0	Gamma Alumina 3.8	Delta Alumina 5.4	Al ₆ Si ₂ O ₁₃ 8.0	CaAl ₂ Si ₂ O ₈ 2.8		NaAlSi ₃ O ₈ 6.9
Alumina Clay					86.0						12.4
Alumina Soil					71.6	Anorthite ^a 18.8	Biotite ^b 6.9		Hercynite ^c 2.7		

a. Anorthite: (Ca,Na)(Si,Al)₂O₇b. Biotite: KMg₃(Si,Al)O₁₀(OH)₂c. Hercynite: FeAl₂O₄

forms prepared with clay or soil are cost effective compared to the waste forms prepared with silica.⁵ Soil- and clay-based glass-ceramics offer an opportunity to incorporate contaminated waste into durable low volume waste forms. The PCT appears to be a viable test for the glass-ceramic waste forms also. However, the effects of particle size distribution, and the glass matrix and crystalline phase distribution on releases are to be investigated.

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Glass-Ceramic

Glass

Calcine

PCT

MCC-1

EA Glass

ARM Glass

Young's Modulus

Chemical Durability

Microstructure

Soil

Waste Forms

Synthesis of glass-ceramics