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IRON PHOSPHATE GLASSES: AN ALTERNATIVE FOR VITRIFYING CERTAIN NUCLEAR WASTES

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EXECUTIVE SUMMARY

A high priority has been given to investigating the vitrification of three specific nuclear wastes in iron phosphate glasses (IPG). These wastes, which were recommended by the Tank Focus Area (TFA) group of Hanford, are poorly suited for vitrification in the currently DOE-approved borosilicate (BS) glasses. They include (1) a sodium bearing waste (SBW) at INEEL, (2) a high chrome waste (HCW) at Hanford, and (3) a high sodium/sulfate waste (HSSW), also known as low activity waste (LAW) at Hanford. A simulated composition for each waste, which was simplified by neglecting components present in quantities < 0.4 wt%, was used in the present investigation.

In the past twelve months covered by this annual report, more than 400 IPG wasteforms (ranging from 50 to 300g) that contained varying amounts of SBW, HCW, or HSSW-LAW were prepared and investigated. The aqueous chemical durability, which is one of the most important properties for determining the suitability of a glass in waste vitrification technology, was measured by three independent techniques for both vitrified and devitrified IPG wasteforms as a function of waste loading. All these methods gave results in excellent agreement with each other. They include (1) direct measurements of the dissolution rate (D_R) of bulk wasteforms in deionized water (DIW) at 90°C, (2) the product consistency tests (PCT) at 90°C, and (3) the vapor hydration test (VHT) at 200°C. The density, thermal expansion coefficient, high temperature viscosity, and the crystallization and liquidus temperatures were also measured for a few selected wasteforms using standard laboratory techniques.

All three wastes were successfully vitrified in iron phosphate glasses attaining a maximum waste loading as high as 40 to 48 wt% for SBW, 70 to 75 wt% for HCW, and about 30 wt% for HSSW-LAW. At this maximum waste loading, the chemical durability of the IPG wasteforms met all current DOE requirements. The solubility of Cr_2O_3 and SO_3 in iron phosphate glasses was about 2.6 wt% and 5 wt%, respectively, compared to < 1 wt% in borosilicate glasses for both oxides. The low solubility of these oxides in borosilicate glasses limits the maximum waste loading to about 20 wt% for SBW, 25 wt% for HCW, and 10 wt% for HSSW-LAW. Based on maximum waste loadings, amounts of additional oxide components required for vitrification, and the solubility of

 Cr_2O_3 and SO_3 , it is estimated that the wasteform volume will be 2 to 4 times less when vitrified in iron phosphate glasses compared to the volume in borosilicate glasses.

The present research is also aimed at obtaining scientific and engineering data required for conducting larger (industrial) scale production of IPG wasteforms. In collaboration with the V.G. Kholpin Radium Institute in Russia and INEEL (Dirk Gombert), small amounts, about 1 kg, of iron phosphate glasses containing 40 and 48 wt% SBW were successfully melted in a Cold Crucible Induction Melter (CCIM). Measurements of the chemical, physical, and thermal properties for the CCIM-melted IPGs are still continuing, but the successful melting of 1 kg amounts of SBW-containing IPG in a CCIM is highly encouraging and suggests that CCIM may be a viable technique for large-scale melting of IPG wasteforms.

In another research collaboration with the Energy and Nuclear Research Institute in Brazil, the feasibility of microwave melting of the IPGs is being investigated. Preliminary results for a few successful, small-scale trial meltings (about 50 g) demonstrate that microwave melting is another method for preparing IPG wasteforms with no foreseeable problems for scaling up the production to larger rates.

Processing IPG wasteforms requires a relatively low temperature (900 to 1100°C) and short times (2 to 6 h) compared to borosilicate glasses. These advantages combined with those of a significantly higher waste loading, and the need for adding only small amounts of other components (for example, HCW can be vitrified in IPG by adding only a source of P_2O_5) can produce a considerable savings in time, energy, and cost for vitrifying the nuclear wastes being investigated in the present study.

1. INTRODUCTION

Vitrification of nuclear waste in a suitable glass is considered the most effective process for waste disposal, and the U.S. Department of Energy (DOE) currently approves only borosilicate (BS) type glasses for such treatment. However, many high level nuclear waste (HLW), presently awaiting disposal, have complex and diverse chemical compositions, and often contain components such as phosphates, sulfates, chrome oxide, and heavy metals that are poorly soluble in BS glasses [1,2]. Such problematic wastes can be pre-processed and/or diluted to compensate for the incompatibility with the BS glass matrix, but this can be an expensive solution and involves risk to the operators. It is more desirable to avoid pre-treating or diluting the waste since these alternatives will greatly increase the wasteform volume and the overall cost for vitrification. Direct vitrification using an alternative glass that uses the major components already present in the waste is preferable since it should minimize the wasteform volume and overall cost.

Our previous studies [3-24] have shown that iron phosphate glasses (IPG) have the potential in vitrifying many nuclear wastes that are either completely unsuitable or poorly suitable in BS glasses in terms of reducing the wasteform volume and disposal cost. The present research is a continuation of our previous work and is focused on three specific wastes that are considered high priority by the Tank Focus Area (TFA) Report of Hanford [1]. The main objectives are to investigate the feasibility of vitrifying these wastes in IPG and to acquire scientific and engineering knowledge that is needed to utilize IPG for vitrifying selected nuclear wastes on a production scale. The feasibility for melting these IPGs by the Cold Crucible Induction Melter (CCIM) technique has also been explored in a preliminary fashion.

2. RESEARCH PROGRESS

At the recommendation of TFA report, the following three types of nuclear wastes are being investigated.

(1) a Sodium Bearing Waste (SBW) at INEEL,

- (2) a High Chrome Waste (HCW) at Hanford, and
- (3) a High Sodium/Sulfate Waste (HSSW) at Hanford, also called Low Activity Waste (LAW)

The composition of these three wastes were simplified by neglecting components present in quantities less than 0.4 wt%. The simplified composition of each waste is given in Table 1. These wastes were chosen primarily because of their high sodium, high chrome, and high sulfate content, all of which can seriously reduce the maximum waste loading in BS glasses [1,2]. The IPGs are expected to have a higher solubility limit for those components based on our previous studies [3-24] and, therefore, potentially higher waste loadings than can be achieved in BS glasses.

For the twelve months covered by this annual report, more than 400 IPG wasteforms (50-300 g samples) containing varying amounts of SBW, HCW, and HSSW-LAW were prepared and investigated. A few selected properties that are critical for long term storage have been measured for the wasteforms. The results for all three wastes are very promising.

Oxide	wt%		
	SBW	HCW^{*}	HSSW-LAW
Al_2O_3	27.8	21.0	4.4
B_2O_3	0.4	-	-
Bi ₂ O ₃	-	3.0	-
CaO	2.2	(CaF ₂) 3.0	-
Cl	0.9	-	0.6
Cr_2O_3	0.2	4.0	0.4
Fe_2O_3	1.4	9.0	-
F	0.8	-	1.6
K ₂ O	7.6	-	-
La_2O_3	-	1.0	-
MgO	0.4	-	-
MnO	0.8	-	-
Na ₂ O	52.3	26.0	75.3
P_2O_5	1.6	5.0	7.7
SiO_2	-	16.0	0.5
SO ₃	3.6	-	9.5
U_3O_8	-	9.0	-
ZrO_2	-	3.0	_
Total	100.0	100.0	100.0

Table 1. Simplified composition, wt%, of the SBW, HCW, and HSSW-LAW.

* Three HLWs of highest chrome oxide content (2.0-4.3 wt%) from clusters 7, 8, and 14 at Hanford [2]) were blended in proportion to the total amount (estimated by Hanford) of waste for each cluster to yield the waste composition given in the column labeled HCW (High Chrome Waste).

2.1. INEEL Sodium Bearing Waste (SBW)

The SBW-containing (up to 48 wt%) IPGs were melted in alumina crucibles at 950-1000°C without problems. These melts became chemically homogenous due to their low viscosity, < 10 poise, resulting a melting time of only a few (1-2) hours. No sulfur rich inclusions or phases were detectable in the IPG when examined by scanning electron microscopy (SEM). From 43 to 100 wt% of the sulfate originally present in the waste was retained in the IPG whose leach resistance was excellent. The chemical durability of IPG containing 40 and 48 wt% SBW (denoted as IP40WG and IP48WG, respectively) was evaluated from the bulk dissolution rate (D_R), the PCT, (7 days in deionized water at 90°C) and from the vapor hydration test (VHT), (7 days at 200°C).

The IP40WG had the best chemical durability. The total normalized amount of Al, Ca, Cr, Fe, K, Mg, Mn, Na, and P released from the IP40WG during PCT was only 1.3 g/L (0.7 g/m²) (Figure 1). The excellent chemical durability of the IP40WG was verified by the VHT results (Figure 2) where the measured corrosion rate for the IP40WG and IP48WG was < 0.2 and 190 g/m²/day, respectively (Table 2). The unofficial DOE standards for PCT release and VHT corrosion rate are 2 g/m² and 50 g/m²/day, respectively. These results indicate that IPGs containing up to 40 wt% SBW satisfy all of the existing requirements for chemical durability.



Figure 1. Normalized elemental mass release (g/L (a) or g/m² (b)) from iron phosphate glasses and standard borosilicate glasses after PCT in DIW at 90°C for 7 days. Elements where the mass release was ≤ 0.01 g/L or g/m², i.e., Ca, Cr, Fe, Mg, and Mn are not shown. The initial (pH_i) and final (pH_f) pH of the leachate is given for each glass.



Figure 2. Optical photographs of the cross section of IP40WG (a) and IP48WG (b) specimens after the VHT (200°C for seven days). No corroded layer was detectable on the surface of the IP40WG glass. The corrosion layers were clearly seen on the surface of the IP48WG samples, but still compares favorably with borosilicate glasses such as LD6-54-12.

Wasteform	Corrosion rate $(g/m^2/day)$
IP40WG	< 0.2
IP48WG	~190
LAW-A33	~140 [27]
LD6-54-12	~196* [27]

Table 2. Comparison of VHT corrosion rates $(g/m^2/day)$ of iron phosphate (IP40WG and IP48WG) and borosilicate glasses [27] at 200°C for 7 days.

* Test conducted at 175°C, higher value would be expected when conducted at 200°C.

The SBW can be vitrified in IPGs at waste loadings up to 48 wt%, but at a loss in chemical durability. The IPGs offer a good chemical durability and a low melting temperature (950-1000°C) for a short time (1-2 h). These advantages including smaller waste volume, excellent chemical durability, lower melting temperature, and shorter melting time will lead to cost effective and safer melting processing and imply that smaller furnaces can be used for the same given output.

2.2. Hanford High Chrome Waste (HCW)

The vitrification of the simulated high chrome waste (HCW) was achieved by simply adding a source of P_2O_5 to the waste and melting the mixture at 1250°C for 2 h. The solubility limit of Cr_2O_3 in these IPG melts is about 2.6 wt%, compared to < 1 wt%

[28] in common BS glasses. IPGs with a waste loading of up to 75 wt% had an extremely good chemical durability as determined by PCT and VHT. The excellent chemical durability was still retained when the IPGs were deliberately crystallized. As shown in Table 3, the total normalized elemental mass release after PCT at 90°C for 7 days was only 1.86 and 1.89 g/m², respectively, for glassy (IP75WG) and crystallized (IP75WX) iron phosphate wasteforms containing 75 wt% HCW.

Element	Normalized elemental		mass release (g/m ²)	
Element	70 wt% Wasteloading		75 wt% Wasteloading	
	IP70WG	IP70WX	IP75WG	IP75WX
Al	0.28	0.22	0.48	0.37
Bi	< 0.01	< 0.01	< 0.01	< 0.01
Ca	< 0.01	< 0.01	< 0.01	< 0.01
Cr	0.01	< 0.01	0.01	< 0.01
Fe	< 0.01	< 0.01	< 0.01	< 0.01
Na	0.54	0.54	0.69	0.73
Р	0.27	0.21	0.39	0.32
Si	0.23	0.35	0.29	0.44
U	< 0.01	0.02	< 0.01	0.03
Total	1.33	1.34	1.86	1.89

Table 3. Normalized elemental mass release (g/m^2) from glassy and crystallized iron phosphate wasteforms after PCT in deionized water at 90°C for 7 days.

In Figures 3a and b, both glassy and crystallized iron phosphate wasteforms containing 70 wt% HCW (IP70WG and IP70WX, respectively) did not have any visible or detectable corrosion layer on their surface after VHT at 200°C for 7 days. Only a thin corrosion layer from 11 to 34 µm thick was observed on the surface of the IP75WG and IP75WX samples, respectively, after VHT. Based on this corrosion layer, the corrosion rate for the IP75WG and IP75WX wasteforms was calculated to be only 3.3 and 14.4 g/m²/day, respectively. Corrosion rates of 140 to 196 g/m²/day have been reported for the LAW-A33 and LD6-54-12 borosilicate glasses (see Table 2).



Figure 3. Appearance of (a) glassy IP70WG and IP75WG, (b) crystallized IP70WX and IP75WX wasteforms after VHT for 7 days at 200°C.

The simulated blend of the three high chrome wastes at Hanford used in the present study (see Table 1) are about 10 wt% of the total HLW at Hanford. Use of IPGs will greatly reduce the volume of vitrified high chrome HLW, which should reduce the overall disposal cost in a major way [2].

A more detailed report on the vitrification of SBW and HCW in IPG, and properties of the wasteforms is given in Appendix 1 and 2, respectively.

2.3. Hanford High Sodium/Sulfate Waste (HSSW-LAW)

IPGs containing up to 30 wt% HSSW have been successfully vitrified at 900-1000°C for 1-2 h. SEM analysis did not reveal any sulfate segregation, inclusions, or nodules in the glass. There was no observable sulfate "gall" layer on the surface of molten IPGs, as is seen for borosilicate melts that contained greater than 1 wt% SO₃ [29]. ICP-ES and XRF analyses indicated that from 40 to 60 wt% of the sulfate originally present in the waste was retained in the IPGs. It appeared that sulfate retention in IPGs was dependent on the melting temperature and time, suggesting a melting condition of \leq 1000°C and \leq 2 h had the highest sulfate retention (~60 wt%). Results show that the IPG wasteforms containing as high as 5 wt% SO₃ do not contain any sulfate "gall" layer on the surface and continue to have an excellent leach resistance.

There are several additives that seem to improve the chemical durability of IPG containing 30 wt% HSSW (IP30WG). These include CaF₂, CaO, Al₂O₃, and Cr₂O₃. The

preliminary results for the chemical durability of IP30WG with different additives are given in Table 4. The substitution of a 3 to 10 wt% of CaF₂, Al₂O₃, or Cr₂O₃ for Fe₂O₃ produces a significant improvement in the chemical durability of iron phosphate glasses containing 30 wt% HSSW.

Types of IPG	PCT at 90°C for 7 days (Total normalized elemental	VHT at 200°C for 7 days (Corrosion rate, g/m ² /day)
	mass release, g/m ²)	
IP30WG	2.2	202
IP30WG + 5 wt% CaF_2	0.7	< 0.2
$IP30WG + 10 wt\% Al_2O_3$	1.2	41
IP30WG + 3 wt% Cr_2O_3	1.3	< 0.2

Table 4. Chemical durability of IPGs containing 30 wt% HSSW with different additives.

2.4. Other Work

The iron phosphate glasses containing 40 and 48 wt% SBW (IP40WG and IP48WG) have been successfully melted in a Cold Crucible Induction Melter (CCIM) at the V. G. Khlopin Radium Institute, Russia, in the amounts of 1 kg each. The chemical composition as measured by ICP-ES for the wasteform melted at CCIM is close to that for the wasteform prepared on a laboratory scale (50-300 g), but contains about 3 to 4 wt% SiO₂. The source of this SiO₂ was the silicon carbide used as sacrificial conductive materials (susceptor) to initiate the melting process. The chemical, physical, and thermal properties of the IPGs melted in a CCIM are being investigated. The successful melting of small amounts of the IP40WG and IP48WG in a CCIM is highly encouraging and suggests that CCIM can be a viable technique for processing large-scale IPG wasteforms.

The microwave melting of IPG also seems feasible, as just recently demonstrated for a few small-scale trial meltings (~50 g, max. power of microwave oven ~1100 W). Microwave melting is easier when the composition contains alkali oxides, such as Na₂O, since alkalies improve the coupling of the batch and microwave energy. Since, most nuclear wastes contain a substantial amounts of alkalies (> 10 wt%), the microwave melting of IPG wasteforms appears to be an alternative method that could be scaled up for larger production rates. The chemical and physical properties for the microwaveprocessed IPGs are now being measured in order to determine whether these properties differ for any reason from the properties of similar glasses prepared by conventional melting. Work is also in progress to melt larger amounts of glass using a larger and higher power microwave oven (furnace).

Lead iron phosphate glasses (LIPG) were also investigated during the past year because of their improved chemical durability. The chemical durability of glassy and crystallized LIPGs containing 14 wt% simulated Hanford B-110 waste was up to 100 times better than that for window glass. The Mössbauer spectra indicated that both Fe(II) and Fe(III) ions were present in all the samples. The Raman spectra for the glasses contained two dominant bands, which were characteristics of pyrophosphate groups, (P-O) stretching mode of P-O nonbridging oxygen at 1074 cm⁻¹ and (P-O-P) sym stretching mode of bridging oxygen at 760 cm⁻¹, respectively.

3. SUMMARY AND PLANED WORK

The present investigation of iron phosphate glass wasteforms has identified several advantages for vitrifying the SBW (INEEL), HCW and HSSW-LAW (Hanford). Among these advantages is a high waste loading of the simulated SBW from 40 to 48 wt%, HCW 70 to 75 wt%, and HSSW up to 30 wt%, depending upon the desired leaching resistance or chemical durability. The chemical durability of these vitrified iron phosphate wasteforms satisfies all known DOE requirements (PCT and VHT). Iron phosphate glasses can be melted as low as 900-1000°C for SBW and HSSW without sulfate segregation, and at 1250°C for HCW (75 wt% waste loading). Because these melts have a high fluidity and become rapidly homogeneous, melting times can be as short as a few hours (< 6 h) compared to the ~48 h needed for borosilicate glasses. The high waste loading, low melting temperature, and rapid furnace throughput (short melting times) of iron phosphate glasses can offer significantly reduced costs of vitrifying the Sodium Bearing Waste, High Chrome Waste, and High Sodium/Sulfate Waste.

The investigation of the chemical, physical, structural, and thermal properties of iron phosphate wasteforms containing SBW, HCW, and HSSW-LAW will continue. The main purpose of this work is to determine practical method for melting IPGs on a scale

that is needed for vitrifying nuclear wastes. Melting experiments using Cold Crucible Induction Melter (in collaboration with the V. G. Khlopin Radium Institute, Russia) and Microwave Melting (in collaboration with Energy and Nuclear Research Institute, Brazilian Nuclear Energy Commission, Brazil) will continue during the next year. The electrical conductivity of these iron phosphate melts will be measured as a function of melt composition and temperature. The work is on schedule and proceeding as planned. No problems are anticipated.

4. PUBLICATIONS

The following papers on iron phosphate glasses have been published during the period covered by this progress report.

- "Electrical Conductivity in Mixed Alkali Iron Phosphate Glasses", A. Mogus-Milankovic, B. Santic, D. E. Day, and C. S. Ray, J. Non-Cryst. Solids <u>283</u> (2001) 119.
- "Iron Redox Equilibrium, Structure, and Properties of Iron Phosphate Glasses", X. Fang, C. S. Ray, A. Mogus-Milankovic, and D. E. Day, J. Non-Cryst. Solids <u>283</u> (2001) 162.
- "Iron Phosphate Glasses: An Alternative to Borosilicate Glasses for Utilizing Certain Nuclear Wastes", G. K. Marasinghe, M. Karabulut, X. Fang, C. S. Ray, and D.E. Day, Ceramic Transaction <u>119</u> (2001) 361.
- 4. "The dc Electrical Conductivity of Iron Phosphate Glasses", B. Santic, A. Mogus-Milankovic, and D. E. Day, J. Non-Cryst. Solids <u>296</u> (2001) 65.
- "Mechanical & Structural Properties of Phosphate Glasses", M. Karabulut, E. Melnik, R. Stefan, G. K. Marasinghe, C. S. Ray, C. R. Kurkjian, D. E. Day, J. Non-Cryst. Solids <u>288</u> (2001) 8.
- 6. "Electrical Property and Redox State in Iron Phosphate Melts", F. Chen, W. Jie, and D. E. Day, J. Chin. Ceram. Soc. <u>29</u> (2001) 26.
- "Structure of Sodium Phosphate Glasses Containing Al₂O₃ and/or Fe₂O₃. Part I", A. Mogus-Milankovic, A. Gajovic, A. Santic, and D. E. Day, J. Non-Cryst. Solids 289 (2001) 204.
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- "Chemical Durability and Structure of Zinc-Iron Phosphate Glasses", S. T. Reis, M. Karabulut, and D. E. Day, J. Non-Cryst. Solids <u>292</u> (2001) 150.
- "Structural Features of Lead Iron Phosphate Glasses", S. T. Reis, D. L. A. Faria, J. R. Martinelli, W. M. Pontuschka, D. E. Day, C .S. M. Partini, J. Non-Cryst. Solids <u>304</u> (2002) 188.
- 12. "Iron Phosphate Glasses for Vitrifying Sodium Bearing Waste", C. W. Kim, D. Zhu, D. E. Day, and D. Gombert, Ceramic Transaction (in press).
- 13. "Solubility of High Chrome Nuclear Wastes in Iron Phosphate Glasses", W. Huang, C. W. Kim, C. S. Ray, and D. E. Day, Ceramic Transaction (in press).
- "Structural Features and Properties of Lead-Iron Phosphate Nuclear Wasteforms",
 S. T. Reis, D. E. Day, and M. Karabulut, J. Nuclear Materials (submitted).

5. PRESENTATIONS

- "Cold-Crucible Design Parameters for Next Generation HLW Melters", D. Gombert, J. Richardson, A. Aloy, and D. E. Day, WM'02 Conference, Tucson, AZ, February 24-28, 2002.
- "Iron Phosphate Glasses for Vitrifying Sodium Bearing Waste", C. W. Kim, D. Zhu, D. E. Day, and D. Gombert, ACerS 2002 Annual Meeting, St. Louis, MO, April 28-May 1, 2002.
- "Solubility of High Chrome Nuclear Wastes in Iron Phosphate Glasses", W. Huang, C. W. Kim, C. S. Ray, and D. E. Day, ACerS 2002 Annual Meeting, St. Louis, MO, April 28-May 1, 2002.

6. COLLABORATIONS

Idaho National Engineering and Environmental Laboratory (INEEL) for investigating the feasibility of vitrifying Sodium Bearing Waste (SBW) in the iron phosphate glasses.

V. G. Khlopin Radium Institute, Russia for studying Cold Crucible Induction Melting technique for upscale melting.

Ruder Boskovic Institute, Croatia for studying the structure of IPGs using Raman spectroscopy.

Energy and Nuclear Research Institute, Brazilian Nuclear Energy Commission, Brazil for investigating Microwave melting technique as an alternative melting process.

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- "Effects of Nuclear Waste Components on Redox Equilibria, Structural Features, and Crystallization Characteristics of Iron Phosphate Glasses," G. K. Marasinghe, M. Karabulut, C. S. Ray, D. E. Day, P. G. Allen, J. J. Bucher, D. K. Shuh, Y. Badyal, M. L. Saboungi, M. Grimsditch, S. Shastri, and D. Heaffner, Environment Issues and Waste Management Technologies IV:Ceramic Transactions, <u>93</u> (1999) 195.
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- 11. "Immobilization of Spent Nuclear Fuel in Iron Phosphate Glass," M.G. Mesko and D.E. Day, J. Nuclear Matls. <u>273</u> 27-36 (1999).

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APPENDIX 1

"Iron Phosphate Glasses for Vitrifying Sodium Bearing Waste", C. W. Kim, D. Zhu, D. E. Day, and D. Gombert, ACerS 2002 Annual Meeting, St. Louis, MO, April 28-May 1, 2002.

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APPENDIX 2

"Solubility of High Chrome Nuclear Wastes in Iron Phosphate Glasses", W. Huang, C. W. Kim, C. S. Ray, and D. E. Day, ACerS 2002 Annual Meeting, St. Louis, MO, April 28-May 1, 2002.

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