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Comparing elemental measurements at packaging and after storage for signatures of chloride salt radiolysis

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Abstract

Radiolysis of hydrated alkaline earth chloride salts by alpha radiation from plutonium produces the chloride containing gases HCl and Cl_2. These gases are known to diffuse out of the plutonium-containing material and contribute to corrosion outside of the convenience container. The alkaline earth elements remain with the plutonium-containing material as oxides or hydroxides. The amount of chlorine within the material after storage will be reduced compared to the amount at packaging. The fraction of the alkaline earth elements that are soluble after storage will be reduced compared to the amount at packaging. These signatures may be observable by comparing the chemical analysis measurements made at packaging and after storage. Comparison of measurements on a single Hanford container shows that the chloride does decrease and the alkaline earth elements have reduced solubility in water. Differences seen with other elements make conclusions difficult.

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Introduction

The Materials Identification and Surveillance (MIS) program's principal concern at this time (spring 2021) is corrosion in the Inner Container Closure Weld Region (ICCWR) of 3013 containers in the Pressure and Corrosion bin originating at Hanford resulting in stress corrosion cracking (SCC).[1-5] A fundamental issue is how to demonstrate that corrosion is no longer occuring or occuring at slow enough rates as to not be a concern. One approach is to establish that the conditions within containers have changed since packaging and they no longer support corrosion. Three conditions have been identified as potential limiting factors: (1) the relative humidity, (2) the atmospheric oxygen partial pressure, and (3) the generation of chlorine-containing gases.[3, 4] Demonstrating that the generation of chlorine-containing gases has changed during storage is difficult because no measurement of the extent of this process was made at packaging and currently no measurements have been made at destructive evaluation (DE). One approach to the problem of establishing that generation of chlorine-containing gases was occuring at packaging and during storage involves establishing whether or not the process changed the packaged material during storage in a way that can be detected. When coupled with measurement of the extent of the process at DE, an assessment of the change in the chlorine gas generation process during storage can be made. Determination of the extent of this process at DE is an effort by the MIS program that is just beginning with samples of material taken at DE to be shipped to Los Alamos National Laboratory (LANL) for evaluation during FY21.[6] This report considers if generation of chlorine-containing gases has left signatures that are observed in elemental characterization at DE when compared to elemental characterization at packaging.

Corrosion of stainless steel 3013 containers by atmospheric gases has been considered possible since the earliest studies by the MIS program.[2, 7, 8] The first unequivocal observation of HCl and Cl2 gases generated by plutonium oxide material with hydrated alkaline earth salt impurities occurred in 2017.[9] Capture of HCl gas by the dimethylamino group of trans-Stilbene, 4-(Dimethylamino)stilbene (DMAS), and by 4-(Dimethylamino)cinnamic acid (DMACA) was detected and quantified using NMR spectroscopy of the reaction products. Capture of Cl2 by addition across the olefinic double bond of trans-Stilbene was also detected and quantified by NMR spectroscopy of the reaction products. The study was carried out in a reaction vessel with a frit separating the plutonium material from the organic reactants thereby ensuring only gases were involved. Rios has observed chlorine-containing gases being generated over extended time periods lasting at least 4.5 years. During that time the amount of chlorine captured represented nearly 40% of the chlorine in the sample. The rate of generation slowed considerably over that time to ~10% of the early rate. Rios has also observed that packaged material which had caused extensive corrosion during storage in a 3013 container did not generate chlorine-containing gases seven years after DE.[10] Thus, it is possible that plutonium oxide material with salt impurities which generates corrosive chlorine-containing gases initially after years in storage may lose it's capability to generate these gases.

The stoichiometry of the reactions that generate chlorine-containing reactions can be written as:

$MCl_2 \cdot xH_2O \rightarrow MO + 2HCl + (x-1)H_2O$

$MCl_2 \cdot xH_2O \rightarrow MO + Cl_2 + (x-1)H_2O + H_2$

$MCl_2 \cdot xH_2O \rightarrow MOHClO + HCl + H_2 + (x-2)H_2O$

$MCl_2 \cdot xH_2O \rightarrow MOHClO_2 + HCl + 2H_2 + (x-3)H_2O$

$MCl_2 \cdot xH_2O \rightarrow MOHClO + \frac{1}{2}Cl_2 + \frac{3}{2}H_2 + (x-2)H_2O$

$MCl_2 \cdot xH_2O \rightarrow MOHClO_2 + \frac{1}{2}Cl_2 + \frac{5}{2}H_2 + (x-3)H_2O$

where M is either Mg or Ca. The hypochlorites have been observered in gamma radiolysis of $MgCl_2 \cdot xH_2O$ and remain with the solid material.[11] The solubility of the reaction products vary. Magnesium oxide is not soluble. CaO reacts with water to form $Ca(OH)_2$ whose solubility is pH dependent with lower solubility as the pH increases. The various hypochlorite reaction products solubility are all pH dependent also with lower solubility as the pH increases. Placing these materials in neutral water will increase the pH and limit the amount of alkaline earth element measured in the solution.

Thus, there are two effects that might be seen when looking at the elemental characterization at packaging and at DE. First, the amount of chlorine in the material should be decreased by a small amount. Second, the amount of Mg and Ca in the leach should be reduced compared to acid dissolution.

Elemental characterization of Hanford material at packaging

Pacific Northwest National Laboratory (PNNL) conducted extensive characterization of sixteen materials that resulted in sixteen 3013 containers, Table 1.[12] Only one of the containers with material characterized in the PNNL report has undergone DE. The container is H004302 which was opened at SRS in 2015. This container had a corrosion category of 3A meaning Suspect pitting > 50 μm on convenience can – pit covered with corrosion product. This corrosion category suggests chlorine-containing gases were generated but perhaps not as much as other materials.

Table 1. Correspondence between the Sample ID in the Tingey and Jones report, the 3013 container ID, and current or planned DE.

Sample ID	3013 container ID	DE ID
B-5680	H003248	
B-5497	H003334	
B-5472	H003744	
B-5439	H003817	
B-5470	H003848	
B-5471	H003870	
B-5457	H003965	
B-5501	H003998	
B-5526	H004005	
B-5495	H004015	
B-5456	H004018	
B-5524	H004052	
B-5534	H004075	
B-5532	H004098	
B-5701	H004271	
B-5703	H004302	FY15DE09

PNNL's characterization included (1) a water leach followed by ion chromatography for soluble anions, (2) a concentrated nitric acid leach followed by dilution and elemental characterization by ICP-MS or followed

by anion exchange to remove plutoniums with elemental characterization by ICP-AES, and (3) a sodium hydroxide/sodium peroxide fusion followed by nitric acid dissolution and dilution with elemental characterization by ICP-MS or followed by nitric acid dissolution then anion exchange to remove plutonium with elemental characterization by ICP-AES. Flouride was measured on the dissolved fusion sample using an ion selectrive electrode after pH adjustment. Plutonium was determined by gamma energy analysis at the Plutonium Finishing Plant at Hanford.

The metals were reported based on the most reliable data as determined by which method resulted in the highest measured concentration. The major constituents were reported as percentages of the total as oxides assuming common oxidation states except for calcium, potassium, and sodium which were reported as a percentage of the chloride. Interestingly magnesium was reported as the oxide even though it is possible that some survived calcination to 750 °C as the chloride or hydroxychloride which are stabilized by KCl and NaCl relative to pure $MgCl_2$.[13-16] Fluorine was reported as percentage of PuF_4, remaining plutonium as PuO_2, and chlorine not associated with calcium, potassium, or sodium as percentage of Cl^-.

The sample ID from the PNNL report is B-5703. This sample was one of four materials in this set that was characterized in duplicate. The duplicate analysis gives some information concerning the reproducibility of the characterization methods. The duplicate samples were for quality control purposes and one duplicate was run for each of four material categories. Sample B-5703 was in the Rocky Flats Oxide (high chloride) category. The data reported by PNNL are given in Table 2.

All elements were determined using the Fusion ICP-AES method except for potassium, sodium, gallium, fluorine, chlorine and plutonium. Potassium and sodium were determined using the Acid Leach ICP-AES method. Mass spectroscopy is the preferred over AES for gallium although the differences between the Acid Leach and the Fusion dissolutions were minor. Fluoride was determined using an ion selective electrode after pH adjustment of a Fusion sample.

Table 2. The analytical results for sample ID B-5703 reported by PNNL. The elements are reported as a percentage of the total as oxides or chlorides. The measured amount of each element for the four analytical methods are given. The analytical method that was used for the final result are indicated in red. Fluorine was determined using an ion selective electrode on a dissolved Fusion sample and is indicated as yellow in the Fusion ICP-AES columns rather than adding additional columns. The total plutonium was determined on three separate samples indicated in yellow. Water is determined by TGA.

Element	Amount	Water Leach	Acid Leach ICP-AES (µg/g of sample)		Fusion ICP-AES (µg/g of sample)		Acid Leach ICP-MS (µg/g of sample)		Fusion ICP-MS (µg/g of sample)	
	%	Anion	B-5703	B-5703 dup	B-5703	B-5703 dup	B-5703	B-5703 dup	B-5703	B-5703 dup
Al_2O_3	0.5		220	267	2870	2000				
$CaCl_2$	0.7		62	44	2600	2400				
CrO_3	2.0		712	785	7570	5710	660	690	1600	1200
CuO	0.1		275	291	700	690	220	220	800	350
Fe_2O_3	1.1		3060	3350	8060	6660				
KCl	5.4		45400	44000	12000	12000				
Ga_2O_3	2.2						14000	15000	16000	17000
MgO	1.7		8710	9530	11400	11700				
MoO_3	0.2		370	378	1400	1000	360	350	1500	1100
NaCl	7.0		27900	27100						
Ni_2O_3	1.0		6980	7000	7430	7260	5500	5200	8300	7600
P_2O_5	0		30	35						
PbO	0		49	52						
SiO_2	0.8		130	130	4000	3900				
SnO_2	0								160	120
WO_3	0.4		171	177	5000	5100	180	180	1700	1700
ZnO	0									
Cl-	2.3	10.2								
PuF_4	3.6				8224	9069				
PuO_2	71.1		65.4%	65.4%	65.4%					
H_2O	0.3									
	100.3									

There are four problems with the data reported in Table 2. One problem is reporting Cl^- without a corresponding cation. The mass balance is close to 100% when reported this way but it is actually more than 2% higher because most of the possible cations have an atomic weight greater than that of chlorine. The second problem is that the total amount of chlorine does not add up to the measured value of 10.2%. The third problem is that the amount of some compounds do not correspond to the measured concentration of the element. This is captured in Table 3 in the following way. The major elements are listed by compound with the percentage reported by PNNL. The measured amount which is the average of the two measurements deemed reliable in Table 2 (in red) is shown in ppm. The cation fraction is defined as the fraction of the compound mass that is due to the cation. For instance, for the compound Al_2O_3, using atomic weights, the mass of the cation is 2x27.0 and the total mass is 2x27.0 + 3x16.0 resulting in a cation fraction of 0.5294. The anion fraction is one minus the cation fraction. The cation ppm is the compound percentage times the cation fraction times 10^4. This should be within 1000 ppm times the cation fraction of the measured amount. Chromium, potassium, magnesium, and tungsten measured concentrations are not consistent with the reported compound percentages.

Table 3. The reported major compounds, the reported concentration of the cations of the major compounds, and the cation concentration calculated from the compound percentage are compared. The oxygen, fluorine, chlorine and plutonium concentrations calculated from the reported compounds are also given. The Element concentration and the Cation concentration are marked in yellow for those elements where the reported concentrations are inconsistent. The percentages of plutonium, the other cations, oxygen, fluorine, and chlorine are given in the bottom row. These sum to 100.1%.

Compound	Amount	Element	Cation fraction	Anion fraction	Pu	Cation	Oxygen	F	Cl
	%	ppm			ppm	ppm	ppm	ppm	ppm
Al_2O_3	0.5	2435	0.5294	0.4706	0	2647	2353	0	0
$CaCl_2$	0.7	2500	0.3609	0.6391	0	2527	0	0	4473
CrO_3	2.0	6640	0.5200	0.4800	0	10400	9600	0	0
CuO	0.1	695	0.7987	0.2013	0	799	201	0	0
Fe_2O_3	1.1	7360	0.6992	0.3008	0	7692	3308	0	0
KCl	5.4	44700	0.5241	0.4759	0	28303	0	0	25697
Ga_2O_3	2.2	16500	0.7439	0.2561	0	16365	5635	0	0
MgO	1.7	11550	0.6030	0.3970	0	10251	6749	0	0
MoO_3	0.2	1200	0.6664	0.3336	0	1333	667	0	0
NaCl	7.0	27500	0.3932	0.6068	0	27521	0	0	42479
Ni_2O_3	1.0	7345	0.7098	0.2902	0	7098	2902	0	0
SiO_2	0.8	3950	0.4676	0.5324	0	3740	4260	0	0
WO_3	0.4	5050	0.7929	0.2071	0	3172	828	0	0
Cl-	2.3		0.0000	1.0000	0	0	0	0	23000
PuF_4	3.6	8646.5	0.7588	0.2412	27316	0	0	8684	0
PuO_2	71.1		0.8819	0.1181	627059	0	83941	0	0
H_2O	0.3								
	100.3				65.4%	12.2%	12.0%	0.9%	9.6%

The fourth problem is reporting calcium as calcium chloride. The calcium measured from the acid leach is approximately 10% of the calcium measured using the fusion dissolution method. Calcium chloride is highly soluble and these two methods should agree if calcium is present as calcium chloride. A calcium compound that is not soluble is calcium fluoride. The material in H004302 is classified by the MIS program as being represented by the 3013 Taxon PyroOx-HN-RF-MiscOx.[17] This material is scrap oxide from pyrochemical processes from Rocky Flats that was shipped to Hanford. Materials from this class of process can contain calcium fluoride impurities from the reduction of plutonium fluoride to produce plutonium metal.[18]

$$PuF_4 + 2Ca^0 \rightarrow 2\ CaF_2 + Pu^0$$

Calcium fluoride was also used to coat molds at Rocky Flats which is another potential source.[19] Calcium fluoride has been observed during DE of 3013 containers by XRD (x-ray diffraction) and EDS (energy dispersive x-ray spectroscopy) of materials in the PryoOx-HN-RF-MiscOx taxon.[20, 21]

In order to arrive at a set of internally consistent values for the PNNL measurements, the compound percentages for chromium, potassium, magnesium, and tungsten were adjusted and the remaining chlorine was assigned to magnesium by adding a new entry for $MgCl_2$. The sum of the magnesium from both MgO

Table 4. Internally consistent elemental results based on PNNL characterization data for sample B-5703. The sum of the plutonium, cations, oxygen, fluorine, and chlorine is 101.7%.

Compound	Amount	Element	Cation fraction	Anion fraction	Pu	Cation	Oxygen	F	Cl
	%	ppm			ppm	ppm	ppm	ppm	ppm
Al_2O_3	0.5	2435	0.5294	0.4706	0	2647	2353	0	0
$CaCl_2$	0.015	54	0.3609	0.6391	0	54	0	0	96
CaF_2	0.5	2500	0.5134	0.4866	0	2567	0	2433	0
CrO_3	1.3	6640	0.5200	0.4800	0	6760	6240	0	0
CuO	0.1	695	0.7987	0.2013	0	799	201	0	0
Fe_2O_3	1.1	7360	0.6992	0.3008	0	7692	3308	0	0
KCl	8.5	44700	0.5241	0.4759	0	44551	0	0	40449
Ga_2O_3	2.2	16500	0.7439	0.2561	0	16365	5635	0	0
MgO	0.8	11550	0.6030	0.3970	0	4824	3176	0	0
$MgCl_2$	2.5		0.2550	0.7450	0	6375	0	0	18625
MoO_3	0.2	1200	0.6664	0.3336	0	1333	667	0	0
NaCl	7.0	27500	0.3932	0.6068	0	27521	0	0	42479
Ni_2O_3	1.0	7345	0.7098	0.2902	0	7098	2902	0	0
SiO_2	0.8	3950	0.4676	0.5324	0	3740	4260	0	0
WO_3	0.6	5050	0.7929	0.2071	0	4758	1242	0	0
PuF_4	2.6	654000	0.7588	0.2412	19728	0	0	8684	0
PuO_2	71.9		0.8819	0.1181	634115	0	84885	0	0
H_2O	0.3								
	100.3				65.4%	13.8%	11.5%	0.9%	10.2%

and $MgCl_2$ was set to the measured concentration. The acid leach calcium was assigned to $CaCl_2$ and the fusion calcium was assigned to CaF_2. The PuF_4 amount was adjusted down to accommodate the remaning flouride. The PuO_2 was adjusted up so the sum of PuF_4 and PuO_2 equaled 65.4%. The results are shown in Table 4. This data can be compared to DE data.

Elemental characterization at DE

Savannah River National Laboratory (SRNL) conducts characterization of 3013 DE material. A dissolution and a leach prepare solutions for characterization. The dissolution uses 12 M nitric acid with 0.1 M HF at 95 °C for 300 minutes (5 hours) followed by addition of boric acid to complex flouride ions which prevents formation of plutonium flouride precipitates. The solution is filtered and elemental characterization by ICP-ES (ICP-ES is also known as ICP-AES). The leach uses deionized water at 90 °C for 180 minutes (3 hours) followed by filtering. Characterization of the leachate uses ICP-ES for metals and ion chromatography (IC) for soluble anions.

Container H004302 was characterized in September, 2015. In 2013 SRNL intoduced a new dissolution procedure that resulted in improved mass balances which could vary from 79% to 108% by the old method. Unfortunately, the mass balance for container H004302 was ~91%, which is the lowest mass balance since the method change. The results of SRNL's characterization is given in Table 5. SRNL made duplicate measurements for each method and the average is reported. For Na and K, the leach and acid dissolutions give nearly the same answer. The sum of the chloride associated with Na and K equals the amount of Cl observed by ion chromatograph so there is no chlorine left over for Ca and Mg. However, this is probably

Table 5. The average of two measurements for the hot water leach and the acid dissolution. The oxygen, chlorine, and fluorine concentrations are calculated from the maximum measured concentration and common stoichiometry.

Element	Cation DE		Pu	Cation	Oxygen	Cl	F
	Leach	acid	%	ppm	ppm	%	ppm
Al	0	371		371	330		
Ca	71	310		310	549		
Cr	12	637		637	588		
Fe	3	3935		3935	1692		
K	35600	37500		37500	0	34047	
Mg	2620	8905		8905	5863		
Na	22600	24500		24500	0	37815	
Ni	207	5305		5305	2169		
Pb	0	172		172	13		
Si	NA	2085		2085	2374		
Cl^-	72200	NA					
F^-	0	NA					0
$PO4^-$	0	NA		0			
Pu	NA	NA	656500		87882		
			65.65%	8.4%	10.1%	7.2%	0.0

the result of measurement uncertainty. Using the reported cations and Cl for Leach #2, the sum of the chlorine calculated assuming common stoichiometry from the measured cations (Ca, K, Mg, Na, and Ni) is less than the reported chlorine indicating that all of the dissolved material could have been originally chlorides. All of the other cations have negligible amounts in the leach. The water leach will not dissolve CaF_2, so no fluorine was observed by SRNL. The sum of plutonium, cations, oxygen and chlorine is 91.4% which is consistent with the mass balance that SRNL reports.

There is no corresponding measurement in the Tingey report for the SRNL hot water leach. As discussed above, the hot water leach appears to dissolve chlorides and essentially nothing else. The calcium in the hot water leach is essentially equivalent to the calcium assigned to $CaCl_2$ in Table 4.

The solubility of the transition metals and lead will be discussed now. All of the reported metal oxides are insoluble in water. The small amounts of Cr, Fe, Ni, and Pb in the leach suggest that the solution pH controls their solubility, Table 6. The concentration in the material is calculated assuming a pH of 8.7 in the last column of Table 6. This value can be compared to the leach value. All values agree very well with the calculated Ni concentration being low. Some of the nickel could be in the material as a chloride which is highly soluble. The majority of the Cr and Fe are probably in the +3 oxidation state. The hydroxides of Cr^{+3} and Fe^{+3} are much less soluble than the hydroxides of Cr^{+2} and Fe^{+2}. A small fraction of the total Cr and Fe in the +2 oxidation state, approximately 1%, would lead to the observations reported in Table 6. The amount of these elements reported by SRNL in other samples analyzed in FY15 were consistent with these observations. The amount of Cr in the leach varied from 6 to 57 ppm, Fe from 0 to 6 ppm, Ni from 0 to 207 ppm, and Pb was always 0 ppm.

Table 6. The solubility of the metals. The molarity in the 30 mL leach sample is calculated from the amount of sample, the volume of the leach and the reported concentration. The OH^- concentration and pH is calculated from Ksp and the metal concentration. Assuming a pH of 8.7, the molarity in the sample and the corresponding concentration in the sample is calculated from Ksp.

Element	Formula	Leach (ppm)	Ksp	Molarity of metal in leach (mole L^{-1})	[OH-] in leach (mole L^{-1})	pH of leach	Molarity of metal in leach at pH 8.7 (mole L^{-1})	Concentration of metal in material (ppm)
Cr	$Cr(OH)_2$	12	2.00E-16	7.69E-06	5.10E-06	8.7	7.31E-06	11
Fe	$Fe(OH)_2$	3	4.90E-17	1.79E-06	5.23E-06	8.7	1.79E-06	3
Ni	$Ni(OH)_2$	207	5.50E-16	1.18E-04	2.16E-06	8.3	2.01E-05	35
Pb	$Pb(OH)_2$	0	1.40E-20	1.61E-08	9.33E-07	8.0	5.12E-10	0

Comparison of elemental concentrations at packaging to DE

The measured amounts of elements are compared in Table 7. All elements are reported in Table 7, but direct comparison is only valid for three of the elements; K, Na, and Cl. A water leach is used by both PNNL and SRNL for the determination of Cl. The acid leach used by PNNL and the acid dissolution used by SRNL are close to the same process. As shown in Table 2, only K and Na were reported by PNNL using the acid leach technique.

Table 7. The measured elements at packaging and DE and their ratio expressed as a percentage. The analytical method used is indicated. NM – not measured; NA – not applicable.

Element	At packaging		DE		Ratio
	(ppm)	Method	(ppm)	Method	
Al	2647	Fusion ICP	370	Acid dissolution	14.0%
Ca	2527	Fusion ICP	310	Acid dissolution	12.3%
Cr	6760	Fusion ICP	637	Acid dissolution	9.4%
Fe	7692	Fusion ICP	3900	Acid dissolution	50.7%
Ga	16365	Fusion MS	NM	Acid dissolution	NA
K	44551	Acid leach	37500	Acid dissolution	84.2%
Mg	11130	Fusion ICP	8900	Acid dissolution	80.0%
Na	27521	Acid leach	24500	Acid dissolution	89.0%
Ni	7808	Fusion ICP	5300	Acid dissolution	67.9%
Pb	51	Fusion ICP	172	Acid dissolution	331%
Si	3740	Fusion ICP	2090	Acid dissolution	55.9%
Cl	102301	Water leach	72000	Water leach	70.6%

We expect some of the chlorine to be lost from the solid material to the production of chloride containing gases. The K and Na are both less in the DE material compared to packaging. One possibility for this is inhomogeneity in the material resulting in non-representative samples. The SRNL sample of the material may have less impurities than the PNNL sample. The sampling method that K-Area uses to provide material to SRNL for analysis is not designed to obtain a sample representative of all material. They typically sample easily segregated powder. The PNNL samples were taken at the same time as moisture measurement samples, after screening and using the same procedure as moisture samples.. Assuming that the K and Na ratios are due to the SRNL sample having less impurities over all but that the composition of the impurities are the same, the SRNL sample had ~87% less impurities. The expected chlorine would then be 87% of 102301 ppm which is 89,000 ppm. The measured amount of chlorine is 72,000 ppm. The amount of chlorine loss from the material is 17000 ppm or 1.7%. The material has 0.3 wt% water. Assuming all of this water was associated with the alkaline earths and resulted in either HCl or Cl_2 gas generation and that all of the chloride gases were removed from the material, the chlorine mass loss would be 1.2 wt%.

Table 8 summarizes the information for calcium and magnesium. Calcium chloride is highly soluble and should dissolve completely in both a water leach and an acid leach. Very little calcium dissolves in the acid leach at packaging which suggests it is not a chloride. There is too small an amount of Ca as chloride to draw any conclusions.

The soluble Mg at DE is assumed to be a chloride and is measured to be 2620 ppm. Our analysis of the PNNL results resulted in 6375 ppm of Mg as the chloride. Applying the 87% correction for having less impurities as discussed above results in 5546 ppm Mg as the chloride. There is an ~2900 ppm further reduction in the Mg as chloride content at DE. A reduction of the magnesium chloride content is expected from radiolysis. The reduction of Mg as chloride at DE is greater than expected from sampling issues. However, the difference in analytical techniques used by PNNL and SRNL makes drawing definitive conclusions difficult. If other containers in Table 1 undergo DE and the same trends are observed, then some confidence in the approach will be possible.

Table 8. Comparison of acid leach/acid dissolution results.

Element	At packaging (ppm)		DE (ppm)	
	Acid Leach	Fusion ICP-AES	Water Leach	Acid Leach
Ca	53	2500	71	310
Mg	9120	11550	2620	8905
Breakdown of Mg as oxide and chloride				
	From Table 4		From water leach and acid leach	
Mg as oxide	4824		6285	
Mg as chloride	6375		2620	

Conclusion

The expected effects of radiolysis of hydrated alkaline earth chlorides when comparing the elemental characterization of material at packaging and at DE are only partially supported. The chlorine content of the material is reduced and when normalized to the smaller amount of impurities the loss is close to expected. The calcium and magnesium characterization have differences in the dissolution methods and uncertainties in the measurements that make solid conclusions difficult, especially when comparing the results for only one material. The results for Mg suggest that some radiolysis of $MgCl_2$ could have occurred. There are fifteen additional materials with packaging characterization avialable for comparison if they undergo DE.

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