

**INVESTIGATION of MIS ITEM 011589A and 3013
CONTAINERS HAVING SIMILAR CHARACTERISTICS**

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August 2006

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**Prepared for the U.S. Department of Energy Under
Contract Number DE-AC09-96SR18500**




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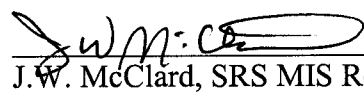
REVIEWS AND APPROVALS


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8/10/06
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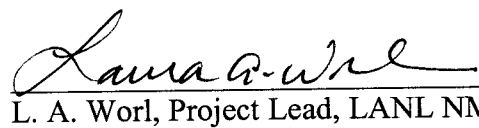
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Executive Summary

Recent testing has identified the presence of hydrogen and oxygen in MIS Item 011589A. This isolated observation has effectuated concern regarding the potential for flammable gas mixtures in containers in the storage inventory. This study examines the known physicochemical characteristics of MIS Item 011589A and queries the ISP Database for items that are most similar or potentially similar. Items identified as most similar are believed to have the highest probability of being chemically and structurally identical to MIS Item 011589A. Items identified as potentially like MIS Item 011589A have some attributes in common, have the potential to generate gases, but have a lower probability of having similar gas generating characteristics.

MIS Item 011589A is an oxide that was generated prior to 1990 at Rocky Flats in Building 707. It was associated with foundry processing and had an actinide assay of approximately 77%. Prompt gamma analysis of MIS Item 011589A indicated the presence of chlorine, fluorine, magnesium, sodium, and aluminum. Queries based on MIS representation classification and process of origin were applied to the ISP Database. Evaluation criteria included binning classification (i.e., innocuous, pressure, or pressure and corrosion), availability of prompt gamma analyses, presence of chlorine and magnesium, percentage of chlorine by weight, peak ratios (i.e., Na:Cl and Mg:Na), moisture, and percent assay. These queries identified 15 items that were most similar and 106 items that were potentially like MIS Item 011589A. Although these queries identified containers that could potentially generate flammable gases, verification and confirmation can only be accomplished by destructive evaluation and testing of containers from the storage inventory.

Introduction

The Materials Identification and Surveillance (MIS) program was established to confirm the suitability of plutonium-bearing materials for stabilization, packaging, and long-term storage under DOE-STD-3013. As part of this program, representative samples of the materials that were packaged to meet the standard are undergoing tests to monitor gas generation and corrosion to verify that the storage package will not be challenged during storage. These tests are performed at the standard maximum limit for moisture content (0.5wt%). Recently, one test item, MIS Item 011589A, exhibited an increase in partial pressure for both hydrogen and oxygen that was inconsistent with other MIS items [1]. The presence of oxygen and hydrogen within a 3013 container is important because it has the potential to produce flammable gas mixtures. The objective of this investigation was to examine the Integrated Surveillance Program (ISP) database and identify items currently in storage whose characteristics are most similar or potentially like MIS Item 011589A. The ISP database contains the available process history, data collected during stabilization/packaging of the containers and any additional assay data (such as prompt gamma) collected after packaging. Prompt gamma provides a qualitative measurement for chlorine, fluorine, magnesium, sodium, aluminum and beryllium. Very few of the containers have chemical analyses.

Methods

MIS Item 011589A is an oxide that was generated prior to 1990 at Rocky Flats in Building 707. It was associated with foundry processing and had an actinide assay of approximately 77%. Prompt gamma analysis of MIS Item 011589A showed the presence of chlorine, fluorine, magnesium, sodium, and aluminum.

To ensure a comprehensive inclusion of any 3013 container that was potentially similar to MIS Item 011589A, an initial target population of oxides was extracted from the ISP database. Two queries were then performed using Microsoft Access and Microsoft Excel to identify items that were either most similar or potentially like MIS Item 011589A (Figures 1 and 2). Items identified as most similar are believed to have the highest probability of being chemically and structurally identical to MIS Item 011589A. Items identified as potentially like MIS Item 011589A have some attributes in common, have the potential to generate gases, but have a lower probability of being similar.

Query 1 included MIS Represented groups that used 011589A for representation [2,3,4]. Some of the MIS Represented groups using 011589A were eliminated from consideration based on further evaluation of process knowledge and one additional group was added that had not previously been associated with MIS Item 011589A. Query 1 also used binning classification (i.e., innocuous, pressure, or pressure and corrosion), availability of prompt gamma analyses, presence of chlorine and magnesium, percentage of chlorine by weight, peak ratios (Na:Cl and Mg:Na), and moisture as evaluation criteria. Query 2 was based on process of origin (i.e., item numbers of the form 010xxx or 011xxx) and, except for percent assay, used the same evaluation criteria as Query 1. Results of these queries are discussed below.

Results and Discussion

Query 1 used represented items [2,3,4] and process knowledge to identify 1,021 containers in the ISP Database (Figure 1) that potentially could be similar to MIS Item 011589A. Included in this population were Hanford (1A, 1E, 2E), RFETS (1B), and SRS (1A, 1D) MIS represented groups (Table 1). Hanford represented group 1E was added based on process knowledge that material in this group was initially composed of about 40% Rocky Flats foundry oxides and about 60% pyrochemical oxides but specific item traceability back to Rocky Flats item numbers was unavailable. SRS Groups 1E and 2A originally used MIS Item 011589A for representation but were eliminated from consideration based on process knowledge as originating from processes and sites that would have been unlikely to generate material similar to MIS Item 011589A.

Next, containers in these represented groups were analyzed in a manner consistent with the methods used for container bin assignments. This approach excluded innocuous items ($n = 166$) that are unlikely to generate gases because they have both low levels of impurities and very low moisture content. Thus, a total of 855 items remained for further evaluation.

Prompt gamma analysis was used to evaluate the presence of chlorine and magnesium and also to calculate peak ratios. Of the 855 containers, 750 had prompt gamma analyses and these were

evaluated for the presence of both chlorine and magnesium. Items lacking both chlorine and magnesium ($n = 422$) were excluded from further consideration because hydrogen generation is unlikely in large amounts (Figure 1). The next evaluation criterion was the quantity of chlorine present. Items having less than 2.0 percent by weight of chlorine ($n = 42$) are most similar to MIS Item 011589A and are considered to be more likely to either generate or at least not consume oxygen. High levels of chlorine usually result in oxygen consumption (corrosion reactions, etc.), and thus, items with greater than 2% chlorine ($n = 286$) were excluded from further evaluation.

The 42 items having less than 2.0 wt% were partitioned into foundry oxides and pyrochemical oxides using prompt gamma peak ratios. Pyrochemical oxides, which are dissimilar to MIS Item 011589A because of their characteristics (i.e., originating process), were defined as having a Na:Cl ratio between 9.5 and 15.5 and a Mg:Na ratio less than 0.25. Foundry oxides, which are considered similar to MIS Item 011589A, were defined as having a Na:Cl peak ratio less than 9.5 or greater than 15.5 and a Mg:Na peak ratio greater than 0.25. Both pyrochemical and foundry oxides and items lacking prompt gamma analyses were then evaluated using moisture criteria. Items having low moisture levels are considered unlikely to generate gasses whereas high levels of moisture are associated with the generation of hydrogen and oxygen. High levels of moisture are defined as levels greater than or equal to 0.05% when measured by loss on ignition (LOI) and greater than or equal to 0.10% when measured by thermogravimetric analyses (TGA), fourier transform infrared spectroscopy (FTIR), or mass spectroscopy (MS).

Application of the evaluation criteria (i.e., MIS represented, binning classification, prompt gamma peak ratios, presence of chlorine and magnesium, chlorine wt%, and moisture) identified 15 items that are considered to be most similar to MIS Item 011589A (Table 2) and 105 items potentially like MIS Item 011589A (Table 3).

Query 2 also targeted oxides ($n = 3,624$) but, instead of using represented items, process origin was applied as the evaluation criterion. Items that had an input item number of the form 010xxx or 011xxx and whose origin was the Rocky Flats foundry prior to 1990 were retained ($n = 379$) and the remaining items ($n = 3,245$) were eliminated from further consideration (Figure 2). From this group, items with IDC Y61 (mixed U + Pu oxides) were eliminated because they are dissimilar to MIS Item 011589A. Any 3013 container that contained at least one of these original input items was included in this analysis as potentially similar to MIS Item 011589A. At Rocky Flats, other material in IDC's 057, 060, 061, U61, Y61, and 083 were mixed together using assay as a primary constraint for the mixing of material to fill a container [5]. This resulted in containers with material similar to MIS Item 011589A mixed with dissimilar material in varying percentages. No restrictions were placed on the percent of material in the containers like MIS Item 011589A.

To eliminate duplicates, items in Query 2 that were also identified in Query 1 by MIS Representation ($n = 283$) were then eliminated from further consideration. Except for percent assay, the remaining 96 items were then evaluated using the same criteria (binning classification, presence of chlorine and magnesium, chlorine wt%, prompt gamma peak ratios, and moisture) that was used in Query 1. Containers with actinide (Pu + Am + Np) percentages greater than 85 wt% contain low quantities of impurities such as chlorine and magnesium, and are less likely to generate gases. These were considered to have originated from the burning of pure metal

at the foundry rather than from burning of skull material which generally would have assays less than 85 wt%. The evaluation of oxides by this query did not identify any items that were most similar to MIS Item 011589A, but found a single item that was potentially like MIS Item 011589A (Figure 2).

Assumptions and Uncertainties

Several assumptions were made during this evaluation because of data gaps, lack of process knowledge and history, incomplete understanding of how gases are generated, and other factors. These assumptions contribute to uncertainties of the results and are listed below.

1. The generation of hydrogen is associated with the presence of chloride (i.e., sodium chloride, potassium chloride, magnesium chloride, calcium chloride) and magnesium. Because large amounts of chlorine typically consume oxygen as a result of interaction with the metal 3013 container wall, it is assumed that chlorine less than 2.0 wt% is more likely to be associated with oxygen generation.
2. Fluoride is also present in the MIS Item 011589A prompt gamma signature but is not known to have any direct relation to generation of oxygen within 3013 containers.
3. MIS Item 011589A is from Rocky Flats foundry oxides and, therefore, pyrochemical salts are not considered similar based on process of origin.
4. Foundry material is associated with prompt gamma Na:Cl peak ratios that are <9.5 or >15.5 and Mg:Na peak ratios >0.25 . Pyrochemical material is associated with prompt gamma Na:Cl peak ratios between 9.5 and 15.5, and Mg:Na peak ratios <0.25 . The prompt gamma peak ratio analysis method is not 100% accurate [6]. Containers identified as pyrochemical by both Na:Cl and Mg:Na peak ratio tests have about a 79% chance of truly being from pyrochemical processes based on statistical analysis of all prompt gamma data using all known process history for the material. Similarly, 62% of containers identified as foundry material were correctly identified relative to the known process histories. Analysis uncertainties arise mainly from three sources; 1) inaccurate or incomplete process histories, 2) mixing of material within a container, and 3) use of prompt gamma count times less than 60 minutes which affects the prompt gamma sensitivity.
5. Both pyrochemical and foundry oxide material may be contained in Hanford (1E) material.
6. The evaluation criteria for moisture were based on the moisture measurement method. If the method was MS, TGA, or FTIR, containers less than or equal to 0.1 wt% are excluded. If LOI was used, containers having a moisture content less than or equal to 0.05 wt% are excluded. The moisture criteria applied herein are arbitrary and have not been substantiated by testing.

The results of this investigation were made using the best available information. It should be noted that the objective of these queries was to identify items that were chemically and structurally similar to MIS Item 011589A based on characteristics contained in the ISP database. However, destructive evaluation and additional testing of packaged 3013 containers are re-

quired to evaluate whether the phenomenon observed in MIS Item 011589A is directly applicable to the storage inventory.

References

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- [4] McNew, Ryan. October 2003. FB-Line Material Representation in the Materials Identification and Surveillance Program, X-TR-F-00003, Revision 0, Savannah River Site, 13 pp.
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TABLE 1. MIS represented items classification and sample identification numbers by location.

Site	MIS Group	Material Description	Process	MIS Samples
Hanford	1A	Product quality Pu oxides from metal oxidation, metal brushing and burning, and stored product oxides from these processes	Metal oxidation	011589A 011608 TS707001
	1E	Impure and scrap oxides from Rocky Flats	Scrap oxide from pyrochemical process, calcination and precipitation of peroxide, and residue processing.	ARF-102-85-114-1 ARF-102-85-223 ARF-102-85-295 ARF-102-85-355 ARF-102-85-365
	2E	Impure and scrap mixed oxides from alloy oxidation	Metal oxidation screenings and PuU oxides.	Metal Oxidation 011589A Oxide Screenings C06032A 0722141 Hydride Oxidation 05501407
RFETS	1B	Process Oxides	Metal Oxidation	011589A 011608 TS707001
SRS	1A	Metal oxidation from Rocky Flats (foundry oxide, 80-85%)	Metal Oxidation	011589A 011608 ARF-102-85-114-1 TS707001
	1D	Burned metal oxides from Livermore (> 80%)	Metal Oxidation	011589A 011608 MT1490 TS707001

TABLE 2. Items identified by Query 1 as being most similar to MIS Item 011589A.

Surveillance Site	3013 Container ID
Hanford	H002809
	H002866
	H003077
	H003931
	H003989
	H004233
Subtotal	6
RFTES	R600793
	R602498
Subtotal	2
SRS	S001105
	S002117
	S002139
	S002187
	S002221
	S002251
	S002277
Subtotal	7
Grand Total	15

TABLE 3. MIS Items identified by Queries 1 and 2 as being potentially like MIS Item 011589A.

Site	3013 Container Identification Number			
Hanford	H001517	H002757	H003639	H004156
	H002237	H002767	H003643	H004232
	H002380	H002775	H003652	H004292
	H002391	H002786	H003664	H004340
	H002410	H002806	H003671	H004436
	H002434	H003323	H003687	H004559
	H002447	H003326	H003690	H004561
	H002462	H003343	H003695	H004567
	H002465	H003356	H003697	H004581
	H002474	H003367	H003705	H004590
	H002524	H003410	H003711	H004611
	H002530	H003413	H003718	H004623
	H002531	H003499	H003731	H004635
	H002534	H003515	H003748	H004637
	H002538	H003523	H003774	H004649
	H002542	H003564	H003847	H004661
	H002546	H003565	H003864	H004681
	H002579	H003569	H003882	H004684
	H002633	H003598	H003898	H004695
	H002657	H003599	H003916	H004699
	H002685	H003604	H003918	
	H002722	H003626	H003940	
Subtotal				86
RFTES	R600060	R600234	R601793	R611398
	R600142	R600718	R602012	
	R600151	R601558	R602245	
	R600178	R601611	R602787	
Subtotal				13
SRS	S002121	S002136	S002203	S002286
	S002125	S002157	S002284	
Subtotal				7
Grand Total				106

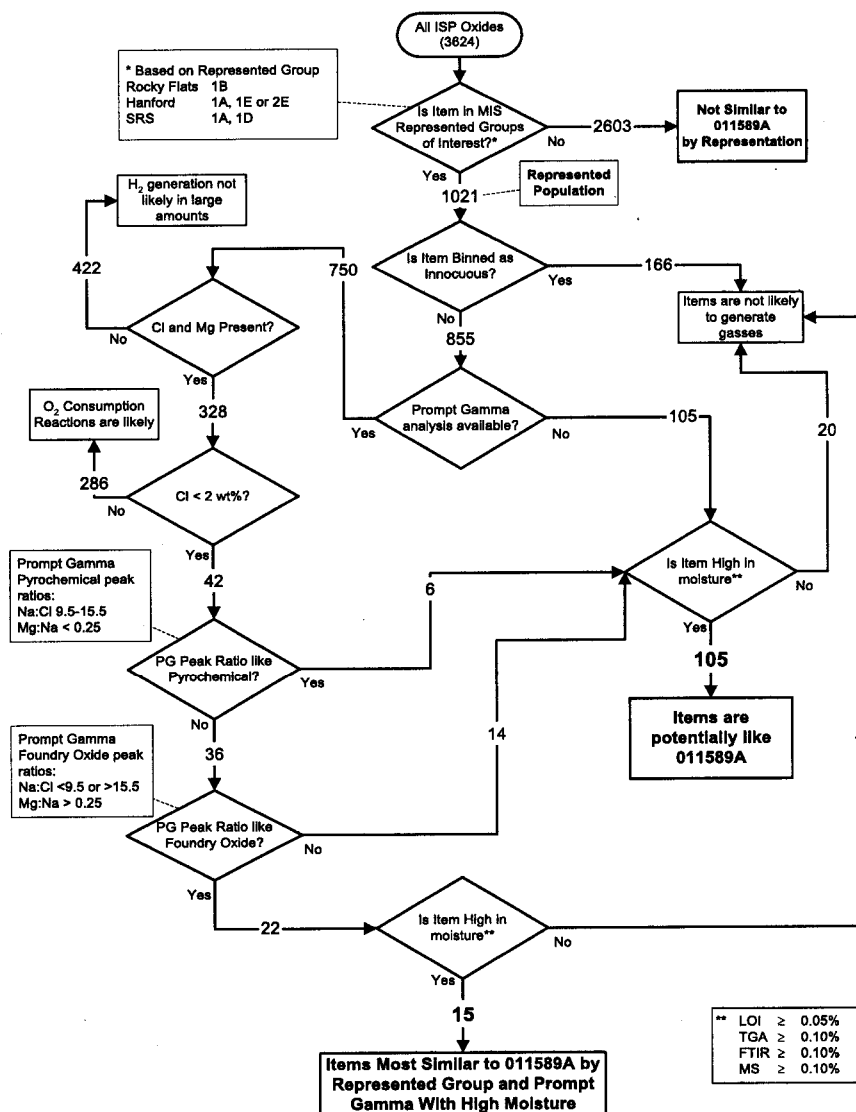


Figure 1. Selection of Items Similar to 011589A By Represented and Prompt Gamma

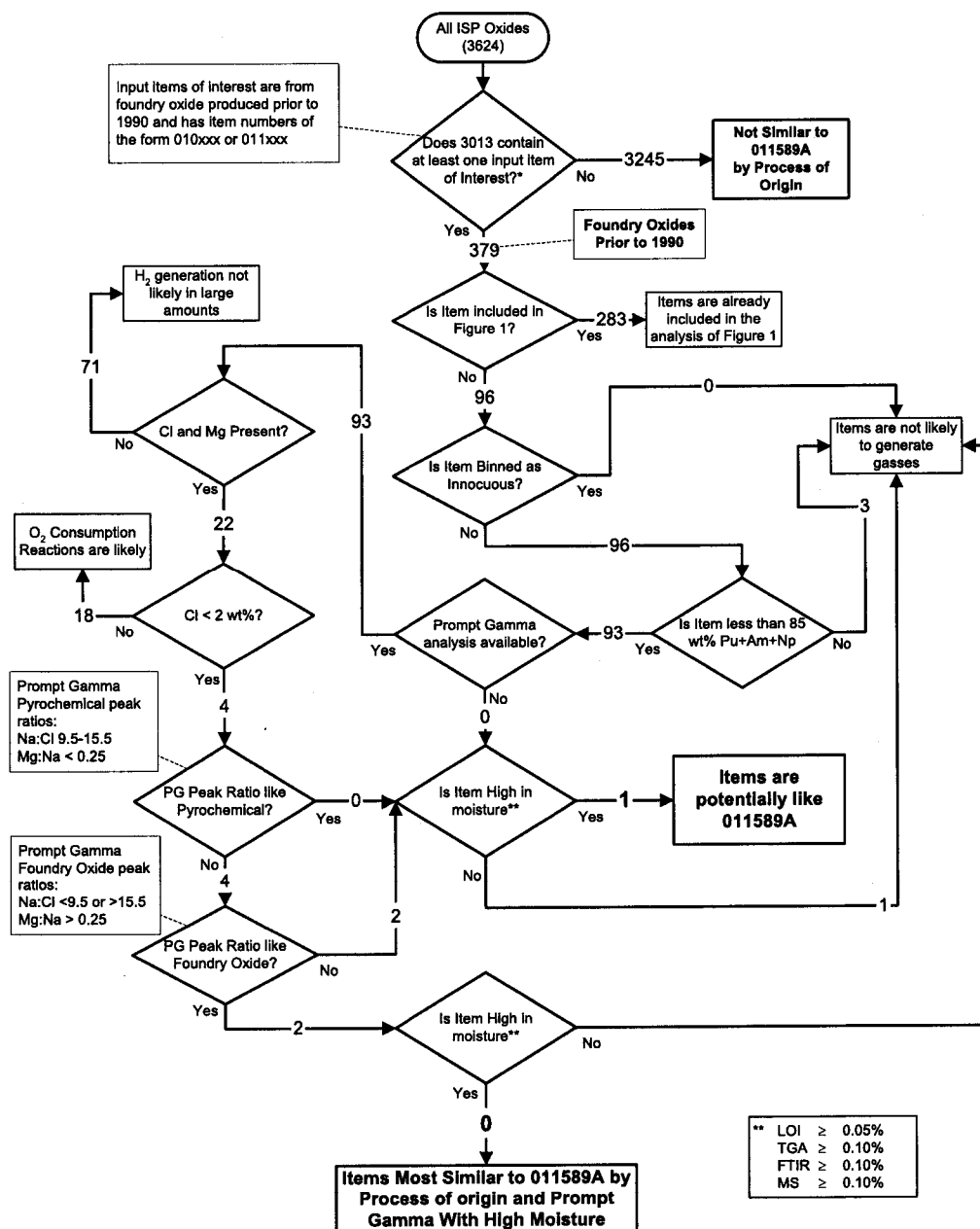


Figure 2. Selection of Items Similar to 011589A By Process of Origin

