

UNITED STATES
NUCLEAR REGULATORY COMMISSION
OFFICE OF FEDERAL AND STATE MATERIALS
AND ENVIRONMENTAL MANAGEMENT PROGRAMS
WASHINGTON, D.C. 20555

March 4, 2014

NRC INFORMATION NOTICE 1999-03, REV. 1: EXOTHERMIC REACTIONS INVOLVING
DRIED URANIUM OXIDE POWDER
(YELLOWCAKE)

ADDRESSEES

All operating uranium recovery facilities that produce uranium oxide powder (yellowcake). All Agreement States with the authority to regulate uranium mills (i.e., Utah, Colorado, Texas, Ohio, Illinois, and Washington).

PURPOSE

The U.S. Nuclear Regulatory Commission (NRC) is issuing this Information Notice (IN) to alert licensees to recent events involving pressurized drums of dried uranium oxide powder (yellowcake). This IN is a revision to IN 99-03 which previously discussed industry experience with pressurized 208-liter (55-gallon) metal drums (hereafter referred to as drums) and related exothermic reactions involving yellowcake material. It is expected that recipients will review this information for applicability to their licensed activities and consider actions, as appropriate, to avoid similar problems. However, suggestions contained in this IN are not NRC requirements; therefore, no specific action or written response is required.

DESCRIPTION OF CIRCUMSTANCES

The NRC is aware of at least nine different sites that have encountered problems with pressurized drums. A brief description of two events is provided below. Both events resulted in uptakes of uranium by workers, and both have similar root causes.

In 2006 at a conventional mill, a worker attempted to open a drum filled with yellowcake that exhibited bulging. Unbeknownst to the worker, the sealed drum was pressurized. The pressure was apparently caused by the generation of oxygen gas within the drum from the decomposition of hydrogen peroxide precipitated yellowcake product. When the drum sealing bolt was loosened, the pressure in the drum caused the lid to blow off the drum and strike the worker. The worker received an uptake of uranium, although the uptake was less than regulatory limits. Records indicate that the drum lid had remained unsealed for three hours after the drum had been filled with yellowcake product, as required by site procedures.

ML14028A175

The facility operator conducted an investigation and identified the root cause as less than adequate procedures. The facility operator concluded that the product did not completely cool, or off-gas, within the three-hour time interval. Corrective actions included revising the applicable procedure to extend the drum sealing interval from three to four hours and providing additional training to site workers.

The second incident occurred in 2012 at a uranium refinery in Canada while workers were opening a drum of yellowcake supplied by an in-situ uranium recovery facility. When a refinery worker loosened the ring clamp on the drum lid, the pressure in the drum (produced by an unexpected build-up of oxygen gas) caused the lid to buckle. The escaping gas ejected approximately 20 kilograms (44 pounds) of dried, powder-like yellowcake material from the drum. The incident resulted in three refinery workers receiving uptakes of uranium. The refinery operator subsequently identified several other drums, supplied by the same uranium recovery facility, which also showed signs of internal pressurization. The uranium recovery facility operator conducted an investigation to determine the causes of the pressure buildup in the drums. The facility operator concluded that the drums became pressurized due to: (1) inadequate cooling and venting of the dried yellowcake product prior to sealing the drum lid; and (2) inadequate drying of the yellowcake product (i.e., inadequate dryer residence time). The NRC later determined that inadequate procedures were contributing causes of the event.

BACKGROUND

The NRC issued IN 99-03 on January 29, 1999, to alert licensees to incidents involving exothermic reactions that occurred after packaging hydrogen peroxide precipitated yellowcake powder into drums. The original IN discussed two types of exothermic reactions—oxygen generation as a byproduct of the drying process and hydrocarbon contaminants reacting with the yellowcake product. At that time, industry took corrective actions which included leaving the drums unsealed for a minimum of three hours and preventing oil and grease from being introduced into the precipitation and drying circuits.

Since 1999, the uranium recovery industry has experienced several more pressurized drum events. Because these events continued to occur, the causes may not be well understood by the industry. Further, past actions taken by industry to prevent pressurized drums may not have been fully effective.

The IN 99-03 also advised facility operators about exothermic reactions of yellowcake with organic materials. These reactions can cause spontaneous combustion of flammable materials such as oil that may enter the process circuit. Refer to Enclosure 1 for an expanded discussion of this hazard.

DISCUSSION

In both the 2006 and 2012 instances, the fundamental cause of the pressurized drums was attributed to the build-up of oxygen gas in sealed containers. The oxygen gas apparently originated from the decomposition of residual uranyl peroxide hydrates or hydrogen peroxide in the dried yellowcake product. Both incidents indicate that the drum lids may have been sealed onto the drums prior to the completion of the uranyl peroxide hydrate decomposition process. Both sites used a minimum three-hour time delay as mentioned in IN 99-03; however, this time delay must have been insufficient based on site-specific operational parameters.

In early 2013, the NRC established a working group to: (1) review the generic implications of the most recent pressurized drum incident including the reasons why drums continue to become pressurized; (2) identify industry experience with pressurized drums; and (3) ascertain whether there were any related trends across the industry. The working group consisted of NRC staff, industry representatives, and subject-matter experts. The NRC used the findings of the working group, as well as information solicited from 14 current and former uranium recovery facilities, in the development of this revision to IN 99-03. As part of the revision process, the NRC is also correcting some of the chemical nomenclature used to describe the thermal decomposition process provided in the original IN. More importantly, as a result of industry experience gained since the NRC issued IN 99-03, this revised IN recognizes a broader range of relevant factors that could result in pressurized drums.

The working group developed a questionnaire that was submitted to various national and international companies having direct experience processing or handling yellowcake. The working group received 14 responses from various entities. The responses were subdivided into two basic categories—sites using ammonia precipitation circuits and sites using hydrogen peroxide precipitation circuits. The survey responses provided the working group with detailed information about dryer and packaging operations at each site as well as industry experience with pressurized drums. If the facilities had experienced pressurized drum problems, the survey asked the respondents to explain the possible causes for the pressurizations. As discussed in Enclosure 1, sites using the ammonia precipitation process with high-temperature calciners have not experienced pressurized drums. Only sites using the hydrogen peroxide precipitation circuits have experienced pressurized drums. Enclosure 3 provides a matrix of the operating parameters for the 11 sites using hydrogen peroxide precipitation circuits and the suspect causes of past drum pressurizations.

The working group concluded that many drum pressurizations were apparently caused by changes in the chemical composition of the yellowcake product after it had been placed into a sealed container. The level of pressurization appears to be related to the cooling and venting time of the product prior to sealing of the drum. The working group determined that the minimum required cooling and venting time for recently dried yellowcake in an unsealed drum depends on the type of dryer, drying temperature, residence time (time product remains in dryer), hold-up time (time interval between completion of drying cycle and when product is placed into drum), dryer feed rate, and product moisture content. These various operational parameters may ultimately contribute to oxygen gas buildup in yellowcake drums.

As noted earlier, multiple operators reported that they had experienced pressurized drum problems, but the specific chemical reactions causing the pressurizations were not always clear. In their survey responses, facility operators provided two general corrective actions to address the pressurized drum issue—increasing the cooling/venting time before the lid is sealed onto the drum and conducting visual inspections of the drums for signs of pressurization prior to shipment. These operators found that increasing the cooling and venting time before sealing the drums and inspecting the drums before shipment appear to have resolved the problem. A range of cooling and venting times was reported, from 4 to 24 hours (see Enclosure 3). In several instances, facility operators chose to extend the cooling and venting times in response to past experiences with pressurized drums. Each facility operator should evaluate their operations and decide how to implement site-specific corrective actions as necessary to prevent pressurized drums.

The working group found that many operators did not measure their product temperature directly, and that discrepancies existed between the maximum dryer temperature and the chemical composition of their final product. It is product temperature, not dryer temperature, which ultimately drives the thermal decomposition process. The working group concluded that, for typical U.S. facilities utilizing hydrogen peroxide precipitation and drying temperatures below 800 degrees Celsius ($^{\circ}\text{C}$) [1472 degrees Fahrenheit ($^{\circ}\text{F}$)], a cooling and venting period of 12 to 24 hours appears sufficient to prevent oxygen gas buildup in yellowcake drums. Above dryer temperatures of approximately 800 $^{\circ}\text{C}$ (1472 $^{\circ}\text{F}$), it is expected that the uranyl peroxide product will be converted to UO_3 (uranium trioxide) product. Oxygen production is not expected to occur after the uranyl peroxide product has been completely converted to UO_3 product. For dryers operating below 800 $^{\circ}\text{C}$ (1472 $^{\circ}\text{F}$), shorter periods of yellowcake cooling and venting prior to securing the drum lid may be ineffective to prevent oxygen buildup in sealed drums.

CONCLUSION

Based on its working group findings and questionnaire responses, NRC concludes that:

- The most likely cause for the drum pressurization events was attributed to continued decomposition of dried uranium product and the production of oxygen after the drums have been filled and sealed.
- For facilities utilizing hydrogen peroxide precipitation and drying temperatures below 800 $^{\circ}\text{C}$ (1472 $^{\circ}\text{F}$), a cooling and venting period of *at least* 12 hours appears to be necessary to prevent oxygen gas build-up in yellowcake drums. Shorter periods may be ineffective. Many operators have elected to implement a cooling and venting time of 24 hours.
- To prevent drum pressurizations, facility operators have implemented two basic corrective actions—increasing the cooling/venting time before the lid is sealed and conducting visual inspections of the drums for signs of pressurization prior to shipment.
- Facility operators should evaluate the potential for organic-based exothermic reactions, as discussed in Enclosure 1. Facility operators should develop protocols to minimize the potential for organics, including oils and greases, to enter into yellowcake process circuits.
- In addition to being industrial and radiological hazards to workers, shipments of uranium yellowcake in packages with internal pressures that reduce the effectiveness of the packages are prohibited by U.S. Department of Transportation regulations. Enclosure 1 provides additional information about these regulations.

CONTACT

This information notice requires no specific action or written response. If you have any questions about the information in this notice, please contact one of the technical contacts listed below.

/RA Aby Mohseni for/

Larry W. Camper, Director
Division of Waste Management
and Environmental Protection
Office of Federal and State Materials
and Environmental Management Programs

Contacts: Robert Evans, Region IV
(817) 200-1234
Robert.Evans@nrc.gov

Ronald Burrows, FSME
(301) 415-6443
Ronald.Burrows@nrc.gov

Thomas McLaughlin, FSME
(301) 415-5869
Thomas.Mclaughlin@nrc.gov

Enclosures:

1. Detailed Technical Discussion
2. Bibliography
3. Survey Results for Facilities Using Hydrogen Peroxide Precipitation
4. FSME Recently Issued Generic Communications

CONTACT

This information notice requires no specific action or written response. If you have any questions about the information in this notice, please contact one of the technical contacts listed below.

/RA Aby Mohseni for/

Larry W. Camper, Director
Division of Waste Management
and Environmental Protection
Office of Federal and State Materials
and Environmental Management Programs

Contacts: Robert Evans, Region IV
(817) 200-1234
Robert.Evans@nrc.gov

Ronald Burrows, FSME
(301) 415-6443
Ronald.Burrows@nrc.gov

Thomas McLaughlin, FSME
(301) 415-5869
Thomas.Mclaughlin@nrc.gov

Enclosures:

1. Detailed Technical Discussion
2. Bibliography
3. Survey Results for Facilities Using Hydrogen Peroxide Precipitation
4. FSME Recently Issued Generic Communications

ML14028A175

RIV:DNMS/RSFS	C:DNMS/RSFS	DD:DNMS	D:DNMS
RJEvans	DBSpitzberg	VHCampbell	AVegal
/RA/	Via email	Via email	Via email
10/24/13	11/06/13	01/02/14	12/31/13
FSME:DMSSA	FSME:DWMEP	DWMEP/DURLD	C:DWMEP/DURLD
ARMcIntosh	RABurrows	TGMcLaughlin	BvonTill
Via email	Via email	Via email	Via email
10/24/13	10/28/13	10/28/13	10/29/13
NSIR	FSME:DMSSA	FSME:DILR	OGC/GCLR/RMR
CGrigsby	DWhite	JCai	TLStokes
Via email	Via email	Via email	Via email
10/28/13	10/24/13	11/05/13	12/17/13
OE/EB	NMSS	DD:DWMEP/DURLD	D: MSSA
TMarenchin	HJGonzalez	DPersinko	JMoses for LDudes
Via email	Via email	/RA/	/RA/
11/14/13	11/08/13	01/24/14	02/28/14
D:DWMEP			
AMohseni for LWCamper			
/RA/			
03/04/14			

Detailed Technical Discussion

At least nine uranium recovery facilities have experienced pressurized drum events. The reasons for these pressurization events varied from facility to facility (see Enclosure 3 for a complete list of suspected causes for the drum pressurizations). The actual causes of previous drum pressurization events are still in question. The causes may include the decomposition of free hydrogen peroxide (H_2O_2) carried over with the dried yellowcake, decomposition of uranyl peroxide product, production of steam from residual water, reaction of uranium compounds with inorganics, or perhaps a combination of these causes. In addition, a reliable and accurate chemical test for free hydrogen peroxide in yellowcake has not been validated which would allow facilities to precisely determine the actual causes for these types of incidents.

The NRC's working group identified several topics that are discussed in detail below. The working group's findings are based on the information that was identified or made available to the group, in part, through uranium recovery facility responses to surveys. Two of the 14 surveys were conducted for sites that are no longer in service, meaning that some of the information presented in the survey may be based on individual recollections versus formal documentation.

Precipitation with Ammonia and Use of a Calciner to Dry Yellowcake

Three facility operators out of 14 reported using ammonia precipitation instead of hydrogen peroxide precipitation. These operators also dried their precipitated product at high temperatures in a calciner. There was no evidence that the ammonia precipitation process, in combination with a calciner, had ever resulted in pressurized drums. Therefore, these types of facilities are excluded from the current discussion about H_2O_2 precipitated product.

The Chemistry of Hydrogen Peroxide Precipitated Yellowcake

Facilities using the hydrogen peroxide precipitation process may create pressurized drums if their operational processes are not appropriately controlled. The chemical product of precipitation depends on the temperature of the solution undergoing precipitation. Based on the survey results, hydrogen peroxide precipitation typically occurs under ambient conditions. At temperatures below $50^\circ C$ ($122^\circ F$), the precipitate is generally of the form $UO_4 \cdot 4H_2O$ (uranyl peroxide tetrahydrate). The final desired product is $UO_4 \cdot 2H_2O$ (uranyl peroxide dihydrate).

Converting the tetrahydrate form ($UO_4 \cdot 4H_2O$) of uranyl peroxide to the desired dihydrate form ($UO_4 \cdot 2H_2O$) occurs quickly under typical drying conditions. For example, laboratory samples of $UO_4 \cdot 4H_2O$ will dehydrate to $UO_4 \cdot 2H_2O$ in about one hour when dried at $100^\circ C$ ($212^\circ F$) (product temperature, not dryer temperature). Typical maximum dryer temperatures at facilities using hydrogen peroxide precipitation range from $130^\circ C$ ($266^\circ F$) to $649^\circ C$ ($1200^\circ F$), with most facilities operating well below $300^\circ C$ ($572^\circ F$). Of course, laboratory studies do not take into account industrial scale production issues such as difficulty in ensuring uniform drying temperature of the product and desired moisture content. The composition of the final product will depend on a variety of drying conditions including dryer temperature, heating time, heating rate, feed rate, product temperature, water content, hydrogen peroxide content, pressure, etc.

As a result of all of these variables affecting the final product, it is likely that other chemical species are forming. The compound $UO_4 \cdot 2H_2O$ does not undergo dehydration like $UO_4 \cdot$

4H₂O, but rather loses oxygen and water simultaneously (i.e., it decomposes to another compound). Uranium trioxide (UO₃) will form at around 500°C (932°F) (product temperature), so for most facilities this reaction is not expected to occur. However, a range of uranium compounds between UO₄ · 2H₂O and UO₃, are likely to form under current typical drying temperatures and drying times. As a group, these intermediate compounds are referred to as amorphous UO_x, where (3 ≤ x ≤ 3.5). While UO₄ · 2H₂O is considered the most stable form of uranyl peroxide, amorphous UO_x is considered unstable with respect to the decomposition to UO₃ even at room temperature. Table 1 demonstrates one example of dryer temperature versus product formation.

Table 1
 Drying Temperature and product composition: Phases identified in hydrogen peroxide precipitated yellowcake dryer product by X-ray diffractometry¹

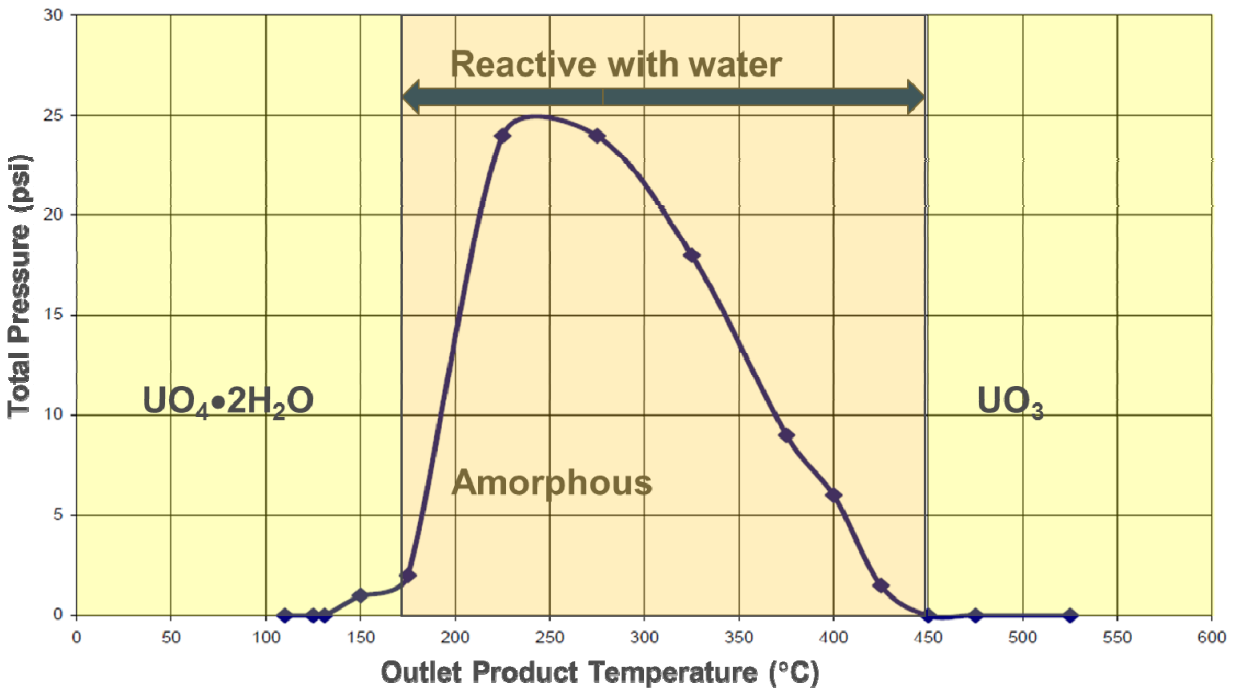
Sample ID	Dryer Discharge Temperature (°C)	UO ₄ ·2H ₂ O	Amorphous UO _x	UO ₃	U ₃ O ₈
001	as-is	X			
015	125	X			
002	131	X			
022	145	X			
016	150	X			
003	175	X			
017	175	X			
004	225	Trace	X		
005	275		X		
006	325		X		
018	375		X		
019	400		X		
008	425		X		
020	425		X		
021	450		X		
023	475		X		
010	525		X	4.30%	
011	575			X	
012	625			X	
014	769				X

¹empty cells indicate not detected

In addition, amorphous UO_x has been reported to react with free water to liberate oxygen gas. It is not clear whether this is a reaction resulting in UO₃, or some other type of reaction. Experiments to date have demonstrated this effect by mixing relatively large amounts of water with amorphous UO_x. Figure 1 demonstrates this phenomenon. It is unknown what effect residual moisture at levels typical of uranium recovery facilities has on amorphous UO_x. It has also been found that neither UO₄ · 2H₂O nor UO₃ react with water in this manner.

Figure 1

Product chemistry: Dried hydrogen peroxide precipitated yellowcake reactivity with water



Addition of Excess Hydrogen Peroxide During Precipitation Process

A stoichiometric excess of hydrogen peroxide is required to optimize precipitation of uranyl peroxide yellow cake. The degree of excess is determined by the composition of the uranium bearing solution (feed stock for precipitation). Molybdenum, vanadium, and other reactive metals contained in the feed stock react with hydrogen peroxide to form soluble complexes. In addition, some fraction of hydrogen peroxide may decompose during the precipitation process. Facility operators should be aware that some of this excess hydrogen peroxide may be carried over into the drying process. The working group understands that an effective drying cycle should eliminate this excess hydrogen peroxide.

Stability of Hydrogen Peroxide in the Presence of Uranyl Peroxide Solids

Precipitation of dissolved uranium by the addition of hydrogen peroxide is a well-known and common process within the uranium recovery industry. It has been demonstrated that this precipitation process is a reversible chemical reaction. One consequence is that an excess of dissolved hydrogen peroxide must be maintained in solution to drive the precipitation reaction to completion and, hence, to minimize dissolved uranium losses in resulting waste streams. The use of excess hydrogen peroxide is a common practice in the uranium industry where the maintenance of low uranium tails in the precipitation process is desired. The filtrate fluids associated with the resulting uranyl peroxide slurry must also contain a modest but finite concentration of dissolved hydrogen peroxide to avoid dissolution of uranyl peroxide solids. As a result, moist uranyl peroxide slurries entering any drying equipment may contain a small but finite concentration of dissolved hydrogen peroxide.

Industrial hydrogen peroxide solutions are relatively stable as long as they are properly stored at moderate temperatures, maintained at a pH below 5, and do not come into contact with impurities, especially metals. Uranyl peroxide solids are typically precipitated at low pH (2-4) under ambient conditions in the presence of small amounts of excess hydrogen peroxide. The resulting slurries are usually pressed and washed at ambient conditions in a filter press operation to remove soluble filtrate impurities from the filter cake. The acidity of the wet cake will likely remain low keeping any residual free hydrogen peroxide relatively stable. This free hydrogen peroxide will, however, begin to decompose over time to oxygen gas and water as it remains in contact with the uranyl peroxide solids. The rate of this decomposition is unknown and, if a test were to be performed to measure residual free hydrogen peroxide, it would have to be performed on fresh uranyl peroxide solids to minimize the subsequent decomposition of hydrogen peroxide. This may explain why it has been difficult to measure free hydrogen peroxide in filter cake samples as the time to perform the tests might be too long for the hydrogen peroxide to remain stable and not decompose.

The other condition under which hydrogen peroxide can decompose is elevated temperature. Hydrogen peroxide will slowly decompose at room temperature. The rate of decomposition will increase as temperature increases. If any free hydrogen peroxide enters the dryer it will likely decompose as the temperature of the uranyl solids increases. However, if the free hydrogen peroxide fails to instantly decompose upon entry into the drying chamber, the residual hydrogen peroxide may be captured in the uranyl peroxide crystalline structure during the drying process. Facility operators should try to minimize the amount of residual free hydrogen peroxide in the product prior to the drying process.

Drying Temperature of Uranyl Peroxide in Rotary Vacuum Dryers

While different dryer types and precipitation processes are utilized in the industry, the majority of facility operators uses hydrogen peroxide precipitation and employs some type of rotary vacuum dryer that operates at a relatively low temperature. These systems are typically batch operations with ambient temperature yellowcake slurry introduced into a pre-heated chamber at atmospheric pressure. The chamber is then sealed and depressurized. The sub-atmospheric pressure within the chamber (i.e., the vacuum) does not remain constant during the drying cycle. Rather, the pressure continuously decreases as water vapor is liberated and evacuated from the chamber via the vacuum pump circuit. The vapor capacity of the vacuum pump limits the operational vacuum (pressure) within the chamber. During the period in which boiling of free moisture is the principle process within the drying chamber, the temperature of the yellowcake solids is tied to the boiling point of water at that pressure. Near the end of the drying cycle, sufficient free moisture has been removed and the pressure within the chamber decreases and approaches a steady state. As this condition is reached, the yellowcake temperature rapidly rises toward the temperature of the heating surfaces within the drying chamber. Essentially, there are two phases to the batch vacuum drying cycle. The first is controlled by the temperature-pressure relationship of boiling water and the capacity of the vacuum pump to remove water vapor. In the second phase, the vacuum pump vapor capacity is no longer limiting and the temperature of the solids is controlled by heat transfer between the vessel surfaces and the yellowcake solids.

Regardless of the temperature of the dryer, there is still a minimum time necessary where moisture is driven off before the yellowcake is heated to above 100°C (212°F), the point where $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ starts to be created. Continued heating of the product can therefore lead to

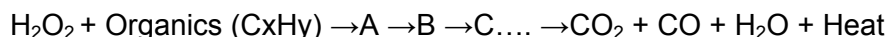
conversion to hydrated UO_4 (uranyl peroxide); however, there is likely limited time for conversion of UO_4 to UO_3 (uranium trioxide). As such, any remaining UO_4 that does not convert to the more stable UO_3 could lead to drum pressurization. Therefore, it is important for facility operators to control the drying process parameters, including temperature, to control product chemistry.

Potential Reactions for Uranyl Peroxide Yellowcake in the Presence of Organic Matter

Five of 11 respondents that used hydrogen peroxide (H_2O_2) precipitation process reported that they have experienced exothermic reactions in yellowcake due to organic contamination, and five of 11 reported that they pay special attention to hydrocarbon contamination.

The reaction of H_2O_2 with organics is a well-known but complex reaction. When H_2O_2 is in the presence of most organic matter, the hydrogen peroxide can react with the organic to form organic peroxide compounds which are usually unstable or can cause the organic to be oxidized, i.e., "chemically burned." When organic peroxide compounds are formed they have been known to detonate, i.e., cause spontaneous combustion or cause oxidation reactions to occur. These latter reactions result in the evolution of heat (from the "burning" of the organics) and the evolution of CO_2 (carbon dioxide), CO (carbon monoxide), and H_2O (water) depending upon the completion of the reaction. When hydrogen peroxide reacts in this way with organics there is always a signature gas evolution which will be indicative of the reaction taking place.

Under certain conditions of temperature, metal catalysts, and reactant concentrations, organics can react with the hydrogen peroxide. This interaction results in a complex, multi-step reaction which typically forms many intermediate hydroxyl radicals as the oxidation reaction is on-going. This process can be simplified as follows:



Where A, B, C, etc. are the intermediate compounds that form prior to full oxidation (compounds that contain OOH^\cdot or OH^\cdot radicals). The end result of this chain of reactions is that the organic is "chemically burned" and the signature off-gases of this reaction are $\text{CO}_2 + \text{CO} + \text{H}_2\text{O}$ plus heat.

When these intermediate compounds form, they combine unstably bound oxygen together with hydrogen and carbon in the same molecule, and these organic peroxides can ignite easily and burn rapidly and intensely. When organic peroxide begins to decompose, the heat produced by its decomposition may not dissipate as quickly as it is generated which can result in increasing temperatures which further intensifies the rate of exothermic decomposition. This can create a dangerous situation known as a self-accelerating decomposition.

When wet yellowcake is introduced into a dryer system it is important that the product not contain organic matter as the reactions of any residual H_2O_2 or decomposed uranyl peroxide hydrate can occur. For trace amounts of organics, this will likely not be an issue as the dryer can dissipate any heat that is formed by these reactions, or the organic will be driven off by the heat of the drying operation. If, however, larger amounts of organics were to be introduced into the dryer, a self-accelerating reaction can occur where the heat cannot be dissipated, high temperatures are generated, and a violent reaction is possible. This has occurred in some dryer facilities when there was a mechanical failure in the dryer which caused large quantities of organics such as oil to be introduced into the dried yellowcake at elevated temperatures.

If the yellowcake is dried at high temperatures as in a calciner, the problem of organic reactions is less likely since the higher temperatures encountered in the dryer will drive off the volatile organics and decompose any organic peroxides that might have been formed. In a low temperature dryer, some organics can remain with the dried uranyl peroxide hydrates and become unstable in the dryer or when removed from the dryer. This could have consequences for drummed material as the decomposition of any organic peroxide can generate heat plus CO₂, CO, and H₂O. The consequence of this could be the slow generation of combustion gases (for small amounts of organics) or a more violent reaction if large amounts of organic peroxides begin to decompose and generate heat which can cause a self-accelerating reaction to occur.

In summary, facility operators should be aware that organic reactions are possible with yellowcake product, and operators should try to locate and eliminate potential sources of organic matter from entering into the precipitation and drying circuits.

Packaging (Drumming) of Yellowcake

Dried yellowcake is almost exclusively stored and shipped in 208-liter (55 gallon) steel drums. In the U.S., the drums must meet U.S. Department of Transportation specifications if the facility operator plans to ship yellowcake material in the drums. Facilities use new drums, reconditioned (used) drums, or a combination of both, depending on drum availability and/or cost. It is critical that operators ensure that drums used to ship yellowcake do not have any organic material (such as oil or grease) in them. Employees must be trained and informed about the serious complications of organic material in drums to ensure that drums used for shipment are received from the suppliers in acceptable condition and the facility does not inadvertently use such drums for another purpose that could result in organic material contamination prior to filling with yellowcake.

Information Notice 99-03 cautioned that new drums and lids could be a potential causal factor in drum pressurization incidents due to the tighter seal of such drums compared to reconditioned drums and lids. The tighter seal could prevent the off gassing from escaping the drum, thereby leading to pressurization. Although this condition is still possible with new drums or reconditioned drums that happen to have better seals, the working group believes that appropriate controls, such as adequate cooling and venting times, will prevent any significant potential for gas build up and drum pressurization.

To limit the potential of shipping a drum of yellowcake that has been pressurized due to an unexpected cause, including a human factor, it is strongly suggested that operators include as part of their final pre-shipment inspection a procedure to check each drum for pressurization. This can be accomplished by a visual inspection of drum lids and a physical check by pushing on the lid and checking for deflection and/or tapping the lid with a rubber mallet to assess deflection and the tone resulting from the tapping. Any drums suspected of pressurization should be returned to the drumming area and carefully depressurized and opened to confirm conditions and causes, if appropriate. Operators should also develop controls to manage the risk of the addition of excess free moisture/water to open drums of product. The working group is aware that one study indicated that pressure is generated from the addition of water into amorphous product. For example, operators should avoid spraying unsealed drums with water to avoid the possibility of adding free water to the dried product.

Shipment of Pressurized Drums

A facility operator who ships pressurized drums may be in violation of U.S. Department of Transportation regulations. In particular, the shipment of pressurized drums may violate regulations 49 CFR 173.24(b)(3) and 49 CFR 173.475(a). Regulation 173.24(b)(3) states that there will be no mixture of gases or vapors in the package which could, through any credible spontaneous increase of heat or pressure, significantly reduce the effectiveness of the packaging. Regulation 173.475(a) states that, before each shipment of any Class 7 (radioactive) materials package, the offeror (the facility operator who offers the drum for shipment) must ensure, by examination or appropriate tests, that the packaging is proper for the contents to be shipped. Based on these two regulations, a standard metal drum may not be the proper package for pressurized uranium product because the pressurization reduces the effectiveness of the packaging. Further, the packaging process may be inadequate if it allows gases and vapors to increase the internal pressure of the package (the drum), resulting in rapid and uncontrolled depressurization when the package is opened.

Facility operators should also be aware of regulation 49 CFR 173.22(a)(4). This regulation requires persons who offer hazardous material for transportation to comply with the manufacturers' instructions for packaging. This regulation applies to drums that have been certified by the Department of Transportation and marked or stenciled accordingly. Many drum manufacturers provide specific instructions for proper closure of the drum, including a requirement to torque the drum seals. Facility operators should be aware of any specific closure instructions provided by the manufacturer or distributor of their certified drums, if these drums are used to transport yellowcake material.

Suggestions for the Uranium Recovery Industry

The working group suggests that the information presented in this IN be supplemented by the uranium recovery industry. The working group suggests that the industry consider expanding the information by determining the chemical species of their product, product temperature versus holding time prior to sealing, impact of excess hydrogen peroxide on the decomposition process, rate of moisture reduction in the dryer, optimum drying parameters (feed rate, temperature, and residence time), and development of procedures and training program to alert workers of the potential risks. For example, facility workers should be made aware that drying is a dynamic process and the change of any process parameter, such as feed rate or dryer temperature, may result in a product that is incompletely dried. Facility operators should use this information to establish site-specific parameters to assure that drum pressurizations do not occur.

Facility operators should consider establishing procedures or other protocols to identify and manage pressurized drums. These procedures should include inspections of the drums for both pressurization and integrity prior to transport. This inspection should be complete even if the drum is stored for an extended period of time prior to actual shipment. Finally, the receiver of shipped drums should also inspect drums for pressurization upon receipt and before opening a sealed drum.

Bibliography

- Boggs, J. E., & El-Chehabi, M. (1957). The thermal decomposition of uranium peroxide, $UO_4 \cdot 2H_2O$. *Journal of the American Chemical Society*, 79(16), 4258-4260.
- Brady, L. J., Susano, C. D., & Lawson, C. E. (1948). *Chemical and physical properties of uranium peroxide*. Report AECD-2366. Oak Ridge, TN: U.S. Atomic Energy Commission, Technical Information Branch.
- Cordfunke, E. H. P. (1961). α - UO_3 : Its preparation and thermal stability. *Journal of Inorganic and Nuclear Chemistry* 23(3-4), 23, 285-286.
- Cordfunke, E. H. P., & Aling, P. (1963). Thermal decomposition of hydrated uranium peroxides. *Journal of the Royal Netherlands Chemical Society*, 82, 257-263.
- Cordfunke, E. H. P., & Van Der Giessen, A. A. (1963). Pseudomorphic decomposition of uranium peroxide into UO_3 . *Journal of Inorganic and Nuclear Chemistry* 25(5), 553-554.
- El-Chehabi, M. (1957). *Decomposition of uranium peroxide*. (Master's Thesis). The University of Texas.
- Gayer, K. H., & Thompson, L. C. (1958). The solubility of uranium peroxide in acidic and basic media at 25 °C. *Canadian Journal of Chemistry* 36(12), 1649-1652.
- Gupta, C. K., & Singh, H. (2003). *Uranium resource processing: Secondary resources*. Berlin: Springer-Verlag.
- Harrington, C. D., & Ruehle, A. E. (Eds.). (1959). *Uranium production technology*. Princeton, N.J.:Van Nostrand.
- Hausen, D. M. (1998). Characterizing and classifying uranium yellow cakes: A background. *JOM* 50(12), 45-47.
- Katz, J. J., & Rabinowitch, E. (1951). *The chemistry of uranium: The element, its binary and related compounds (Part I)*. New York, NY: McGraw-Hill Book Company, Inc.
- Leininger, R. F., Hunt, J. P., & Koshland, D. E. (1958). Composition and thermal decomposition of uranyl peroxide (Paper 69). *Chemistry of uranium: Collected papers, TID-5290, Book 2 (704-721)*. Oak Ridge, TN: U.S. Atomic Energy Commission Technical Information Service Extension
- Merritt, R.C. (1971). *The extractive metallurgy of uranium*. Golden, CO: Colorado School of Mines Research Institute.
- Metzger, R., et al. (1997). Solubility characterization of airborne uranium from an in-situ uranium processing plant. *Health Physics* 72(3), 418-422.
- Moore, R. L., & Watts Jr., R. A. (1952). *Production of UO_3 by calcination of uranyl peroxide*, Document No. HW-26531. Richland, WA: Hanford Works.

- Patton, F. S. (1963). *Enriched uranium processing*. New York, NY: Macmillan Co.
- Rich, R. L. (2007). *Inorganic reactions in water*. Berlin: Springer-Verlag.
- Rodgers, C., & Dyck, B. (2012). Uranium peroxide precipitate drying temperature relationships. *CIM Journal* 3(3), 149-156.
- Sato, T. (1961). Uranium peroxide hydrates. *Die Naturwissenschaften* 48(21), 668.
- Sato, T. (1963). Preparation of uranium peroxide hydrates. *Journal of Applied Chemistry* 13(8), 361-365.
- Sato, T. (1976). Thermal decomposition of uranium peroxide hydrates. *Journal of Applied Chemistry and Biotechnology* 26(4), 207-213.
- Silverman, L. & Sallach, R. A. (1961). Two uranyl peroxides. *Journal of Physical Chemistry* 65(2), 370-371.
- Thein, S. M., & Bereolos, P. J. (2000). *Thermal stabilization of $^{233}\text{UO}_2$, $^{233}\text{UO}_3$, and $^{233}\text{U}_3\text{O}_8$* , Report ORNL/TM-2000/82. Oak Ridge, TN: Oak Ridge National Laboratory.
- Walenta, K. (1974). On studtite and its composition. *American Mineralogist* 59, 166-171.
- The data for Table 1 comes from "Laboratory Characterization of Dryer Test Products," Cameco Corporation, Gerhard Heinrich, John Krause, Mike Murchie, November 2009.
- The data for Figure 1 comes from "Laboratory Characterization of Dryer Test Products," Cameco Corporation, Gerhard Heinrich, John Krause, Mike Murchie, November, 2009 but was adapted and updated for a presentation to the CNSC: "Rabbit Lake UOC Drying Process," Cameco Corporation, Kirk Lamont, November 2012.

Survey Results for Facilities Using Hydrogen Peroxide Precipitation

Time in Dryer (hours)	Dryer Temp (°C)	Yellowcake Temp (°C) When Barreled	Cooling and Venting Time (hours)*	Percent (%) Moisture in Dried Yellowcake	Have You Experienced Any Drum Pressurizations?	Suspected Causes of Drum Pressurizations
12-16	232	Not measured	>12	0 – 1.5 Limit of 2	No	
18-20	164	130	24-72	<1	Yes	Decay of residual H ₂ O ₂
36-48	160	160	24	<1	Yes	Not determined
21-22	163	138	24	1-8, Typically 3-5	Yes	Moisture vaporizing (steam)
6	130	<80	Described as “minimal”	<2	No	
16-20	235	Not measured	>12	0.5-1.5 Limit of 2	Yes	Decay of H ₂ O ₂ and sealing drums too soon
4.5-6	649	66	Previously 3, changed to 24	1-4	Yes	Cooling time and drying time too short
6	371	< 371	4	“no moisture”	Yes	Decay of H ₂ O ₂
Unknown	Not given	Unknown	“a number of hours”	Not measured	Yes	Excess H ₂ O ₂ added during precipitation
20-30	150	<90	12	1-4 w/w	Yes	Hot yellowcake added to moist drum
1.5	245	80	>3	0.5-2.0	Yes	Unknown

* Cooling and venting times are current times, or the most recent times for facilities that are no longer in operation. Several sites increased their cooling and venting times in response to previous pressurized drum events or in response to IN 1999-03.

List of Recently Issued Office of Federal and State Materials and Environmental Management Programs Generic Communications			
Date	GC No.	Subject	Addressees
11/15/2013	IN-2013-22	Recent Licensing Submittals Containing Personally Identifiable Information	All materials licensees, certificate holders, applicants, and other entities subject to regulation by the U.S. Nuclear Regulatory Commission for the use of source, byproduct, and special nuclear material. All Radiation Control Program Directors and State Liaison Officers.
10/17/2013	RIS-2013-17	Resuming Normal Interactions Between the NRC and NRC Stakeholders Following an Agency Shutdown	All U.S. Nuclear Regulatory Commission (NRC) licensees, certificate holders, permit holders, and applicants; all Agreement and Non-Agreement States, and State Liaison Officers; and other interested stakeholders.
10/09/2013	RIS-2013-16, Supp. 1	Interactions Between the NRC and NRC Stakeholders During a Lapse of Agency Appropriations	All U.S. Nuclear Regulatory Commission (NRC) licensees, certificate holders, permit holders, and applicants; all Agreement and Non-Agreement States, and State Liaison Officers; and other interested stakeholders.
10/01/2013	RIS-2013-16	Interactions Between the NRC and NRC Stakeholders During a Lapse of Agency Appropriations	All U.S. Nuclear Regulatory Commission (NRC) licensees, certificate holders, permit holders, and applicants; all Agreement and Non-Agreement States, and State Liaison Officers; and other interested stakeholders.
09/16/2013	IA-03-02	Criteria for Reporting Cybersecurity Incidents	All Radiation Control Program Directors and State Liaison Officers. All Increased Controls (IC) materials licensees. All licensees possessing Category 2 and higher materials.

List of Recently Issued Office of Federal and State Materials and Environmental Management Programs Generic Communications			
Date	GC No.	Subject	Addressees
09/11/2013	RIS-2013-14	Reporting Transactions Involving Temporary Jobsites to the National Source Tracking System	All industrial radiography and well logging licensees, and all Radiation Control Program Directors and State Liaison Officers
Note: This list contains the six most recently issued generic communications, issued by the Office of Federal and State Materials and Environmental Management Programs. A full listing of all generic communications may be viewed at the NRC public Web site at the following address: http://www.nrc.gov/reading-rm/doc-collections/gen-comm/index.html			