Health & Safety Considerations for the Storage, Handling & Application of Persulfates

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Our Presenter

Brant Smith, Ph.D., P.E.
Director of Technology
Evonik Corporation
brant.smith@evonik.com

Outline

- Health & Safety
  - Fundamental Concepts
  - Persulfate
    - Characteristics
    - Decomposition
    - Storage
    - Handling
  - Reductants
  - Summary

Reports of H&S Incidents from the Field will be used to Illustrate Concepts

Fundamental Concepts

- Environmental reagents are capable of reacting with and destroying some of the most recalcitrant and unreactive compounds known to humans.
- These reagents are often delivered to a site as a dry powder
- In order to unleash the reactive potential…
- ….just add water….

Fundamental Concepts

- Dry reagents = stability (most reagents need aqueous phase to react)
- Appropriate amounts of water: Reactions can occur, but rate of reaction is concentration limited and heat can be absorbed by water

- Small amounts of water can be severe problem:
  - Reactions can proceed
  - Dissolves reagents to near theoretical maximum solubility resulting is rapid kinetics
  - Not enough water to absorb heat released
  - Close proximity to solid reagents = easy to maintain high concentrations
  - If it evaporates it can result in clumping of soluble products

Example: Klozur CR

- Due to ability to generate oxygen, both PermeOx® Ultra and Klozur® CR come in vented packages
  - For drums/buckets, water can enter through ports on top of lids
    - Must prevent standing water on top of drums/buckets

- Klozur® CR is an all-in-one product: Contains activator and oxidant
  - Addition of moisture can initiate reaction
  - A few reports people that have stored Klozur® CR pallets outside, in rain which resulted in decomposition reactions
    - Off venting of gas has been observed. Expected to be oxygen.
      - PermeOx® Ultra decomposition is endothermic
      - Product often consumed and forms large solid blocks that will require disposal

Fundamental Concepts

- Heat
  - Makes chemical reactions go faster
  - Temperatures above normal can result in:
    - Autoignition
    - Flammability
    - Phase shift (solids becoming liquids; liquids become gases)

- Heat can be generated a lot of ways:
  - Chemical reaction (acid/base; oxidant/reductant; etc)
  - Heat of hydration (NaOH, CaO, etc)
  - Site activities
  - Solar radiation
  - Electrical resistance
  - Generating electricity
  - Ambient conditions

Example: The Night the Package Material Burned

- Report:
  - Emptied Sodium Persulfate Supersacks were left out overnight in thunderstorm
  - Crews arrived next morning to find Supersack material (woven polypropylene) **partially burnt/smoldering**
    - Flash Point: >500°F (260°C)
    - Autoignition Temperature: 735°F (390°C)

- Exact cause unknown
  - Persulfate decomposition ~750°C?
  - Heat of hydration of CaO (~572°F/~300°C)?
  - Lightning? Other?

- Recommendations: Make sure supersacks are completely empty and properly disposed of at end of day

Fundamental Concept: Incompatible/Reactive Materials

- Acids and bases

- Oxidants and:
  - Reductants
  - Fuels
  - Transition metals
  - Oxidizable organics and other oxidizable compounds

Compounding Effect:

Water + Heat + Reactive Material

Activators and Catalysts

Are often incompatible or reactive with the oxidants

Need to be stored separately

Example: Concentrated Oxidant and Reductants

- Early Field Incident
  - Crystalline thiosulfate was being added to a bucket of Sodium Permanganate solution (up to 40%)
    - Purpose: Neutralize oxidant
  - Concentrated reductant with concentrated oxidant
  - Rapid exothermic reaction caused water to flash to steam which caused worker to be sprayed with 40% Sodium Permanganate
- Result:
  - Several contractors started banning use of solid state reductants from being used to neutralize oxidants

Exhibit 3-2. Cotton Pants Worn by IT Laborer

Marvin, Bruce; D-47, Battelle Chlorinated, 2010

DOE/ORO-2103, October 2000

Fundamental Concepts

- Chemical Compatibility: Chemicals react with certain compounds <u>but not others</u>

- Common uses of chemical compatibility:
  - Identifying Personal Protective Equipment (PPE)
  - Wetted materials contacting solutions
  - Any material contacting reagents

<u>Chemical Compatibility Guides:</u>

- **Manufacturer**
- **Compass Guide to Chemical Resistance**
- **Cole-Parmer and other online resources**

Fundamental Concepts

- Engineering Controls are better than personal protective equipment (PPE)
- Engineering Controls: Removes the risk
- Personal Protective Equipment: Creates a barrier between the person and the risk

Example: Engineering control-Supersack Nozzle

- Supersack nozzle can be placed so that it is inside a tank or other device to minimize dusting

Discharge nozzle/spout

Courtesy of Cascade

Housing for nozzle and control iris

Nozzle opens within tank with reagents flowing into water

Courtesy of XDD/LEA

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Fundamentals: Summary

- Pay attention to:
  - Water
  - Heat
  - Chemical Reactions
  - Material Compatibility
  - Protection of people and the environment

- Response
  - Training
  - Engineering Controls
  - PPE

Persulfates

Persulfate – Safety & Handling

- Evonik supports and practices all tenets of Responsible Care® as Prescribed by the American Chemistry Council

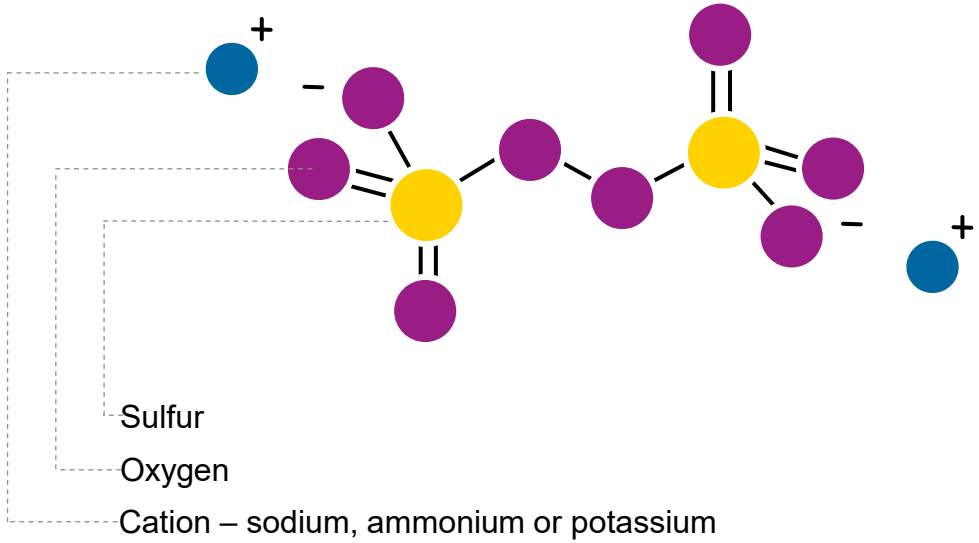
Evonik Persulfates are Manufactured in Tonawanda, NY

	Ammonium	Potassium	Sodium
Physical Form		Crystalline	
Molecular Weight	228	270	238
Crystal Density (g/cc)	1.98	2.48	2.59
Loose Bulk Density (g/cc)	1.05	1.3	1.12
Odor	None	None	None
Color	Off-white	Off-white	White
Solubility in Water (% w/w @ 25°C)	45.9%	5.6%	42.2%
Active Oxygen (%)	6.98	5.90	6.68
pH @ 1%	5.2	6.4	6.0

What are Persulfates?

- The peroxydisulfate (persulfate) anion is the most powerful oxidant of the peroxygen family of compounds.
- It is a free radical generator used in polymerization reactions.
- It is a metal oxidizer and can be catalyzed by transition metals.
- It reacts differently under various pH conditions.

100s of Millions of Lbs of Persulfate are produced and safely used each year



Persulfate – Safety & Handling

Persulfates Can Be Used Safely!!

- Do not Become Complacent
- Read All SDS Data
- Follow Handling Procedures
- Train Employees
- Use Proper Engineering Controls
- Use Proper PPE
- Properly Materials
- Communicate between Team and Local Authorities

Product Health and Safety

- **Low risk is not no risk**
  - Proper techniques, handling, training and PPE are always required
  - We do not consider our products inherently unsafe. But they can become unsafe if not properly handled by trained staff
    - Most safety concerns expressed would apply to all other reagents in the market
- Risk increases with less training and unaware individuals

Slips, Trips and Falls are often the leading health hazard while onsite

Electricity, pressure and worker exhaustion were my primary H&S concerns

General Concerns with Oxidants/Persulfate

- People/Animals
  - Oxidize organics including tissue upon contact (skin, eyes, throat, lungs, etc)
    - Irritation, burns, respiratory issues, etc

- Environment
  - May intensify a fire
  - Persulfate decomposes to form acid
  - Solid peroxides can decompose to form oxygen gas which can build up pressure if confined

- Incompatible Materials
  - Persulfate is a powerful oxidant that will react with various reduced compounds including reduced metals, fuels and other organic compounds

Decomposition

Decomposition

- A triggered event (reaction) which becomes self propagating due to chemically stored energy being released as heat when persulfate breaks down.
- Triggers
  - Heat
  - Moisture
  - Contact with: metals, halides, alkalis, other oxidants, combustibles, organics, reducing agents, ammonia solutions, acids, salt solutions, and cleaners.
  - Combinations of Incompatible Materials can initiate Decomposition

Any contact with incompatible material can initiate decomposition

Contaminant treatment is decomposition, but occurs within the subsurface with diluted persulfate

Decomposition: Onset Symptoms

- Possible starting at ~ 350°F / ~ 180°C
  - Starts to effervesce with acid-like odor and smokes
  - **Emits noxious fumes of SO_x**
  - Can reach temperatures up to 750°C
- AP also emits NO_x
- May form high temperature melt that flows like lava and can ignite nearby combustibles on contact.
- Upon cooling can form solid sulfate salts.
- Fire intensity is increased by heat and oxygen liberated during the decomposition event.

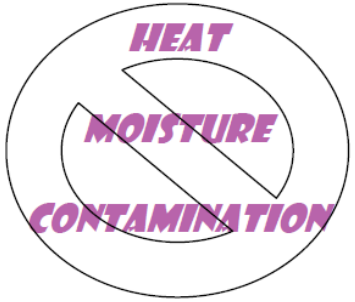
- O_2 lowers flash points of combustible materials.

Persulfate can autodecompose above ~350°F / ~180°C, react with incompatible materials, supply oxygen to a fire, form acidic liquids or gases upon decomposition

Emergency Responders/Halting a Decomposition

- Emergency Responders:
  - Persulfate decomposition will require emergency responders wearing:
    - Full protective rubber clothing
    - Face and head protection
    - Selfcontained breathing apparatus (SCBA).
  - Outside agencies (fire departments, EMTs, etc.) need to be aware of persulfates characteristics and its hazards prior to responding to an incident.
- Halting Persulfate Decomposition:
  - Apply LARGE amounts of water
    - 2 to 8 lbs of H_2O per pound of persulfate (~120 g/L to ~425 g/L)
  - Too little water will intensify the reaction and increase acid mist concentration
  - CO_2 and other gas filled fire extinguishers have no effect
  - Storage in contained areas enhances control of the melt and fire fighting efforts

Preventing Decomposition



- Avoid moisture.
  - Lowers onset temperature.
- Separate from incompatible materials.
  - Reducing agents, acids, bases (alkalis), halides and salt solutions, organics, ammonia solutions, other oxidizers and cleaners.
- Do not store by point sources of heat.
  - Steam pipes, electrical appliances, heating vents, gas flames, welding sparks, radiant heaters, or at temperatures ≥ 113°F/45°C.
- Do not grind or dry mix in equipment that develops frictional heat.
- Do not introduce contamination to persulfate

Store in a cool and dry environment

- Less than 25°C/77°F is recommended
- Not to exceed 45°C/113°F
- Do not store for extended periods of relative humidity is greater than 70%

Example: Possible Persulfate Autodecomposition Event

- Hot Work Permit issued weld component of hopper that contained sodium persulfate
  - Welding temps start at 1700°F
  - >> 350°F where persulfate can autodecompose
- Within minutes “smoke” was observed from top of hopper
- Contractor immediately stopped work, contacted fire department
- No one was hurt and the application resumed

Safe Storage, Handling, and Use of Persulfates

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Persulfate – Safety & Handling

- Persulfates and their solutions can be safely stored and handled.
- Written procedures should be in place and personnel treated to handle persuflate safely.
- Properly dispose of spilled material, and prevent contamination.
- Material that has been wetted or spilled must be isolated and disposed of properly.
- To remove and transport persulfates from the shipping containers, use clean and dry plastic or stainless steel scoops, shovels, pails, etc.
- Cleanliness is essential.

Safe Storage Guidelines

- Store in dry, cool and well-ventilated place
- Store in a manner that is secure from unauthorized personnel
- Avoid contamination
- Avoid formation of dust
- Keep away from food, drink and animal feeding stuffs
- Storage areas have proper egress

- Do not store:
  - Near acids, bases, or reducing agents
  - Near potential sources of fuel / combustible materials
  - Near sources of heat, sparks and open flame
  - At temperatures above 45°C/113°F

- Always follow applicable regulations
  - USA: NFPA 430 guidelines (www.nfpa.org); Code for the Storage of Liquid or Solid Oxidizers

Preferred Storage Conditions

- **Temperature**
  - **Less than 25°C / 77°F**
- **Dry/Relative Humidity**
  - **Less than 60%**
- **Secured**

Common Persulfate Storage

	Ready to Use	Short Term	Moderate Storage	Long Term Storage
Method	Package Material	Under Tarps	Large Tents Connex Boxes	Permanent Warehouse/Storage Structure
Conditions	Exposed to Elements	Modest protection from precipitation	Good protection from precipitation	Best protection from elements
Assessment	Up to Operator to gauge conditions and limit risks	Can still become wet. Potential for heat buildup. No climate control	Little to no climate control. Potential for heat buildup.	Potential for climate control

Expected Field Temperature and Potential for Inclement Weather and their Impact on Storage when Scheduling Field Events

NFPA 400 Guidelines for Storage

	Non-sprinklered	Sprinklered
Building limit thousands of pounds	400	4,000
Pile limit		
in thousands of pounds in 2,310 pound skids of 55 pound bags in 2,200 pound Intermediate bulk containers	40 17 18	400 173 181
Maximum pile height	8 feet or 2 skids	12 feet or 3 skids
Maximum pile width	16 feet or 4 skids	24 feet or 6 skids
Maximum distance from any container to a working aisle	8 feet	12 feet
Minimum distance to next pile (ft)	Aisle width equal to pile height	Aisle width equal to pile height
Minimum distance to wall	4 feet	2 feet
Minimum distance to incompatible material	12 feet	8 feet

Always conform with local, State and Federal Regulations for your area

Persulfate Handling Considerations

Klozur® Persulfates Materials of Compatibility

Recommended:

- 304 and 316 stainless steel for all mixing, conveyance, and storage equipment (tanks, pipes, etc.)

Compatible:

- PVC, polyethylene, Plexiglas®, Teflon®, Neoprene, butyl rubber, glass, FRP (fiber reinforced plastic), EPDM, Fiberglass – specifically vinyl ester resin, Polyester

Incompatible:

- Aluminum, Brass, Buna N, Carbon steel, Copper, Iron, Galvanized pipe/steel (includes zinc-plated materials)

Corrosion rates increase at higher persulfate concentrations

System design should include management of potential pressure build up due to the decomposition of oxidant slurries or solutions. This commonly includes pressure relief values in lines sections that can be closed, vents or administratively.

Elastomers:
Long Term Duration: Teflon or PTFE, PVDF, Gylon®

Short Term Duration: EPDM

For Safety gear: butyl rubber, neoprene

Example: Aluminum Fittings

- Aluminum (Aluminium if you are in the UK) is a common material used in conveyance systems that can be mistaken for stainless steel

- Can be oxidized by persulfate resulting in a yellowish color

Online image of Aluminum Sulfate

Photo provided from field

Personal Protective Equipment

Eye Protection:	Chemical Goggles and Face Shield
Respiratory:	Dust Respirator - NIOSH N95
Hands:	General Purpose Neoprene Gloves
Clothing: and full-	Ordinary work clothes with long sleeves length pants (no cotton)
Protective Clothing:	Approved chemically resistant suite (*e.g.* Tyvek Coveralls), as needed
Footwear: (neoprene)	Shoes with Chemical Resistant Soles

Always refer to the SDS for Details

Example: Glove Selection

25% Caustic was reported to have unknowingly migrated behind works gloves for “an extended period of time” resulting in skin corrosion

- **Engineering controls**
- **Change out gloves**
- **Permeation??**

- Check glove ratings
  - Degradation
  - Permeation/Breakthrough in Minutes

- Resource:
  - Cole Parmer “Safety Glove Chemical Compatibility Database”
- Example: Nitrile Gloves
  - 50% NaOH

MATERIAL	OVERALL RATING	DEGRADATION RATING (@30MIN)	PERMEATION BREAKTHROUGH BY MINUTES
Nitrile	G - Good	E - Excellent	180

First Aid

Avoid possible contact, but if persulfate contacts:

- Eye Contact:
  - Flush with water for at least 15 minutes.
- Skin Contact:
  - Wash with plenty of soap and water. Wash clothing before reuse.
- Inhalation:
  - Get fresh air. If breathing difficulty or discomfort occurs, obtain medical attention.
- Ingestion:
  - Drink one to two glasses of water. Do not induce vomiting.

- All instances: **<u>If irritation occurs and persists, obtain medical attention</u>**

Always refer to the SDS for Details

Eyewash and Showers

- Per OSHA:

Installed and portable emergency eyewash units must be capable of delivering not less then 0.4 gallons (1.5L) of clean water per minute. Portable eyewash units must be capable of delivering water continuously for at least 15 minutes. The water must be readily available to wash both eyes simultaneously. When there is more than one flushing stream of water, flushing streams must rise to approximately equal heights. The eyewash units must be designed to provide flushing water velocities which are not injurious to the eyes and must be designed to provide enough room to allow the eyelids to be held open with the hands while the eyes are in the water stream(s). The nozzles must be protected to prevent freezing of flushing water in cold weather. Also, the nozzles must be protected with airtight covers, which can be easily removed, to prevent airborne contamination. The portable units must be constructed of material that will not corrode in the presence of the flushing fluid.

- From our SDS for Klozur Caustic:

Skin Contact:

Wash off affected area immediately with plenty of water for at least 15 minutes. Get medical attention if any discomfort continues.

Not OSHA Compliant.
Emergency Use

If Properly Charged and Maintained, can be compliant

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Disposal of Persulfates

- Persulfate Crystals
  - Never discard in trash bins
  - Classified as a hazardous waste, oxidizer (40 CFR 261)
    - European equivalents (European List of Wastes LoW)

- Emptied Packaging
  - Residual material left on packaging materials may be termed “non-classified” waste
  - Allows spent packaging to be disposed of in regular waste
  - If concerned about residuals, packaging can be:
    - Rinsed prior to disposal
    - Placed inside compatible plastic bags prior to disposal

Disposal (continued)

- Persulfates which are incidentally spilled on the floor, or otherwise contaminated, are best dissolved in copious amounts of water.
- Large persulfate spills should be handled as a solid hazardous waste.
- Spent persulfate solutions may be diluted with large quantities of water and disposed via treatment systems if legally approved.

Additional Site Safety Considerations

- Additional safety and handling considerations
  - Consider stresses and fatigue of workers (i.e. heat and cold)
  - Take care in lifting bags and handling drums or totes– ergonomics
  - Take care in handling large super sacks
  - Take care in opening bags
  - Take care whenever applying any solution under pressure
  - Make sure all equipment is in proper working condition
  - Make use of GFCIs and grounding of electrical equipment, if needed
  - Comply with Federal, State and local regulations

Other H&S Examples

List of Other H&S Incidents: ISCO

- Persulfate (SP) In tank decomposition
  - Left wetted solid persulfate in bottom of tank overnight with activator (inadvertent)
  - Metals analysis consistent with aluminum alloy
- Alkaline activated persulfate: Chemical Spray
  - Injection system failure
- In ground decomposition at high SP concentrations
  - Keep soil mixing applications at less than 10% without special consideration
- Boiled water in tank with activator combined with persulfate after ~ 8 hrs
- Packer failure
  - Field technician was not wearing PPE, received caustic burn
- Failure at bottom of tank
  - Brass fitting corroded
- Other H&S Issues:
  - Dissolving solid NaOH
    - Exothermic release (boiled water)

Reductive Products

- Headspace gas build-up
  - Reductive products decompose to form various gases (hydrogen, organics, etc) and consume oxygen
  - Careful with confined spaces

- Storage Matters
  - Stored in rainstorm and left exposed for period of time
  - Smoldering product and package material. Pictures look like compost.

- Particle Size
  - OSHA: 420 microns or smaller is a “combustible dust”

Best Practices and Summary

Best Practices

- Properly store persulfate
  - Cool, dry environment away from heat source and incompatible materials
- Batch persulfate in a manner where worker exposure is limited (dust control) and the crystalline persulfate is dissolved at less than 425 g/L quickly
- Always have secondary containment and control possible release pathways
- Be prepared to handle and properly dispose of spills
- Have excess water available

Best Practices

- Evaluate all wetted parts or other parts that may come into contact with reagent to make sure they are chemically compatible
- Make sure there is proper PPE available
- Make sure there are H&S stations including first aide and ability to provide proper eye wash and shower for employees that contact reagents.
- Have shade and potentially climate control environments available for workers and reagents

Summary

- We work in remote and difficult conditions
  - Heat, rain, and cold
  - Generated power with temporary electrical lines
  - Slip, trip and fall hazards
  - High pressure injection systems
  - Large powerful equipment
  - Thermodynamically powerful chemicals
  - Often limited timeframes

- …Yet, 10,000s Remedial Applications have occurred safely

Remedial Projects Have Been and Will Continue to be Implemented Safely

Starts with the People:

Good Decisions, Information, Resources, and Communication

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Conclusion

- Persulfates can be used safely
- As with any chemical, treat them with RESPECT
- Follow proper handling procedures
- Train employees
- Notify responders that persulfates are on site

For More Information Consult the SDS and NFPA Code 430

Europe: CLP & REACH Regulations

Other Applicable Local, State and National Regulations

Please contact Evonik Directly

www.Evonik.com/remediation

Questions?

Brant Smith, P.E., Ph.D.
Director of Technology
Soil & Groundwater Remediation
Evonik Corporation
E. brant.smith@evonik.com

Josephine Molin
Technical Manager, ISCO
Soil & Groundwater Remediation
Evonik Corporation
E. Josephine.molin@evonik.com

Evonik Corporation
Soil & Groundwater Remediation
remediation@evonik.com
www.evonik.com/remediation


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