ERDC/EL TR-18-5

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Evaluation of Sulfide Emissions from a Hydraulic System at the Blue River Dam

Victor F. Medina, Michelle Wynter, Carina Jung,
Amber Russell, Timothy Paulus, and Chris S. Griggs

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Abstract

Hydrogen sulfide releases occurred during a routine maintenance process in a hydraulic oil system at Blue River Dam, Oregon. The project worked under the hypothesis that the sulfide emissions most likely resulted from reductive biological processes. Hydraulic oil samples were collected from the Blue River Dam, and from two other nearby dams with similar hydraulic systems, Hills Creek Dam, and Cougar Dam. Water samples from the reservoir were also collected. Sulfur was found in all the oil and water samples, however, no patterns with sulfur to other parameters (such as percent water or acid neutralization number) were found in the oil samples. A microscopic review of hydraulic filters did not show any evidence of bio-film accumulation. The use of sulfate reductive bacterial genetic probes did not find any microbial activity expected to form sulfide. These results rejected the hypothesis that the sulfide production was from microbial activity. The Authors now hypothesize that the sulfide reaction was from abiotic reactions of an additive, Zinc Dialkyldithiophosphate (ZDDP).

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Preface

This study was conducted by the U.S. Army Engineer Research and Development Center-Environmental Laboratory (ERDC-EL). The project was funded by the Portland District (NWP) under “Work Unit 33143” to support a board of inquiry (BOI) investigating hydrogen sulfide release from a hydraulic oil system at Blue River Dam, Oregon.

At the time of publication, Dr. W. Andy Martin was Chief of the Environmental Engineering Branch, Mr. Warren P. Lorentz was Chief of the Environmental Processes and Engineering Division, and Dr. Elizabeth Fleming was the Director of EL.

COL Bryan S. Green was Commander of ERDC and Dr. David W. Pittman was the Director.

Unit Conversion Factors

Multiply	By	To Obtain
degrees Fahrenheit	(F-32)/1.8	degrees Celsius
feet	0.3048	meters

Acronyms and Abbreviations

Acronym	Meaning
ACC	American Chemistry Council
ASTM	American Society for Testing and Materials, International
BOI	Board of Inquiry
BLR	Blue River Dam (Used as a sample identifier)
CAS	Chemical Abstract Services
CGR	Cougar Dam (Used as a sample identifier)
cm	centimeter
DNA	Deoxyribonucleic acid
DoD	Department of Defense
EL	Environmental Laboratory
ERDC	Army Engineer Research and Development Center
EPC	Environmental Chemistry Branch
EPE	Environmental Engineering Branch
FP	Flash Point
g	Gram
g/L	Grams per Liter
HCR	Hills Creek Dam (Used as a sample identifier)
HPU	Hydraulic Power Unit
IDLH	Immediately Dangerous to Life or Health
ISO	International Organization for Standardization
Kg	kilogram
L	liter(s)
LC50	Lethal Concentration 50
LEL	Lower Explosive Limit
mg	milligram

mL	milliliter(s)
MSDS	Material Safety Data Sheet
MW	Molecular Weight
ng	nanogram
NIOSH	National Institute of Occupational Safety and Health
NWP	Portland District
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limit
PDS	Product Data Sheet
ppmv	part per million based on volume (gas concentration)
QAP	Quality Assurance Plan
REL	Recommended Exposure Limit
S	Sulfur
SRB	Sulfur Reducing Bacteria
STEL	Short Term Exposure Limit
UEL	Upper Explosive Limit
USACE	United States Army Corps of Engineers
USEPA	United States Environmental Protection Agency
VG	Viscosity Grade
VI	Viscosity Index
ZDDP	Zinc Dialkyl Dithiophosphate
μg	microgram
μS	microsiemens

1 Introduction

1.1 Purpose of the study

In 2016, hydrogen sulfide (H_2S) emissions were found during the maintenance of a hydraulic system at the Blue River Dam, Oregon. Hydrogen sulfide is potentially toxic and explosive, therefore, determining the cause of this gas is needed. Three possibilities were considered most likely – the thermal transformation of Zinc Dialkyl Dithiophosphate (ZDDP), a sulfur containing additive to the hydraulic oil, abiotic hydrolysis reaction of the ZDDP, or the microbial mediated reduction of sulfur. This project, conducted by the U.S. Army Engineer Research and Development Center (ERDC) and supported the Portland District (NWP), contains studies that explore sulfide in the hydraulic oil and associated water. The ERDC also explored for evidence of sulfur reduction by microbial activity. The goal was to narrow down the possible causes of this sulfide gas, particularly exploring the hypothesis that the sulfide generation was due to microbial activity.

1.2 Sulfur forms

1.2.1 Elemental sulfur

Sulfur can exist in several forms. Elemental sulfur refers to it in its purist state. Elemental sulfur is typically a yellowish powdery solid and has a charge of zero (0). However, it typically is reactive and forms oxidative and reduced states.

1.2.2 Sulfate

Sulfate is the oxidized state of sulfur. Its typical form is SO_4^{2-}, and its charge is +6. Sulfur dioxide is another oxidized form of sulfur with a charge of +4, but it is not common in aqueous systems. Sulfate is usually non-problematic, although it can be associated with sulfuric acid (see section 1.2.4).

1.2.3 Sulfide

Sulfide is the reduced form of sulfur. It is commonly found dissolved in water as hydrosulfide ion (HS-) and has a charge of -2. Sulfide is also the form found in the toxic gas hydrogen sulfide (H_2S). Sulfide gas is highly offensive smelling at low concentrations. Sulfide gas has a characteristic "rotten egg odor" at airborne concentrations of 0.02 part per million based on volume (gas concentration) (ppmv) (Nicholson and O'Brien 2001). Sulfide gas actually becomes odorless at higher concentrations because it paralyzes the olfactory system. However, as concentrations increase, hydrogen sulfide becomes increasingly toxic and potentially explosive. Table 1 summarizes H_2S toxicity.

Table 1. Hydrogen Sulfide toxicity and explosive characteristics (sources: Nicholson and O'Brien 2001; NIOSH 2005).

Effect/Regulation	Concentration/Temperature
Olfactory Detection (rotten egg odor)	<0.02 ppmv
Recommend Exposure Limit (REL) – A level recommended by the National Institute of Occupational Safety and Health (NIOSH) for adoption by the Occupational Safety and Health Administration (OSHA) as a new permissible exposure limit (PEL) level	10 ppmv (10 minutes)
Permissible Exposure Limit (PEL) – An enforceable exposure limit established by OSHA. Time Weighted Average based on an 8-hour work period.	20 ppmv, 50 ppmv 10-minute peak
Immediately Dangerous to Life and Health (IDLH) – A NIOSH defined concentration where life and health is immediately endangered if exposed.	100 ppmv
Lethal Concentration 50 (LC50) (rat, 1-hour)	713 ppmv
Lower and Upper Explosive Limits (LEL–UEL)	4.3 to 46%
Flashpoint (FP) – the lowest temperature the chemical can form an ignitable mixture in air.	-82.4 °C/-116.3 °F
Auto-ignition Temperature – The lowest point a chemical will ignite in a normal atmosphere without an ignition source.	232 °C/ 450 °F

Hydrogen sulfide is heavier than air with a vapor density of 1.36 grams per liter (g/L). This means that the gas will commonly concentrate in low lying areas and depressions making ventilation of the gas challenging in some instances.

1.2.4 Sulfide/sulfate cycling

When sulfur forms are subjected to cyclic reductive and oxidative reactions, the results are usually detrimental. Reductive reactions form sulfides, that then form sulfide gas (H_2S), (described in section 1.2.3). This gas is toxic and explosive.

When hydrogen sulfide becomes exposed to oxygen, it can react to form sulfate. In water, this reaction forms sulfuric acid (Equation 1)

$$H_2S + 2O_2 = SO_4^{2-} + 2H^+ \quad (1)$$

These acids can irritate breathing tissues and the eyes. In addition, acid forming reactions can cause corrosion problems. If the sulfate is reduced again, issues with hydrogen sulfide can again arise.

1.2.5 Organic sulfur

Sulfur can also be incorporated into organic compounds referred to as organic sulfur. Total sulfur refers to all forms of sulfur in a given aqueous system, this includes organic and inorganic forms:

Total Sulfur = Elemental Sulfur + Sulfate + Sulfide + Organic Sulfur

To account for differences in molecular masses, molar concentrations can be used. However, molar values are often not very intuitive. An alternative is to convert concentrations to mg/L or mg/kg as sulfer (S), as shown in Equation 2

$$X\ mg/L\ as\ S = Y\ mg/L\,x\ \left(MW_{Sulfur} / MW\right) \quad (2)$$

Where *X* is the concentration as S, *Y* is the concentration of the actual molecule of interest, MW_{sulfur} is the molecular weight of sulfur (32 g/mol) and the molecular weight (MW) of the actual compound (96 g/mol for sulfate and 33 g/mol for sulfide).

1.3 Dams studied in this project

This project studied samples from three dams in Oregon: Blue River, Hill Creek, and Cougar. Blue River Dam, was the site of the sulfide release event. Samples from Hill Creek Dam and Cougar Dam, two other dams with similar hydraulic systems were also taken and tested. All of these dams are in relatively close proximity to each other and are part of the Willamette Valley Project, a flood control project consisting of 13 smaller dams (Figure 1) that are operated by the United States Army Corps of Engineers (USACE) Portland District (NWP).

Figure 1. The Willamette Valley Project with locations of dams and facilities. Dams in this study are circled in bright red. (base map from USACE, http://www.nwp.usace.army.mil/Locations/Willamette-Valley/).

1.3.1 Blue River Dam

The Blue River Dam is a flood control dam built in 1968 and operated by the USACE (Figure 2). The Blue River Dam forms a six mile long impoundment on the Blue River and is located in west central Oregon.

Figure 2. Blue River Dam, Oregon.

1.3.2 Cougar Dam

Cougar Dam, built in 1963, is located on the South Fork of the McKenzie River and forms the Cougar Reservoir. It is primarily a flood control facility, but it does have hydropower production. Cougar Dam has a similar hydraulic system to Blue River Dam, and it uses the same hydraulic oil (Chevron Rando® HD, see section 1.9.3).

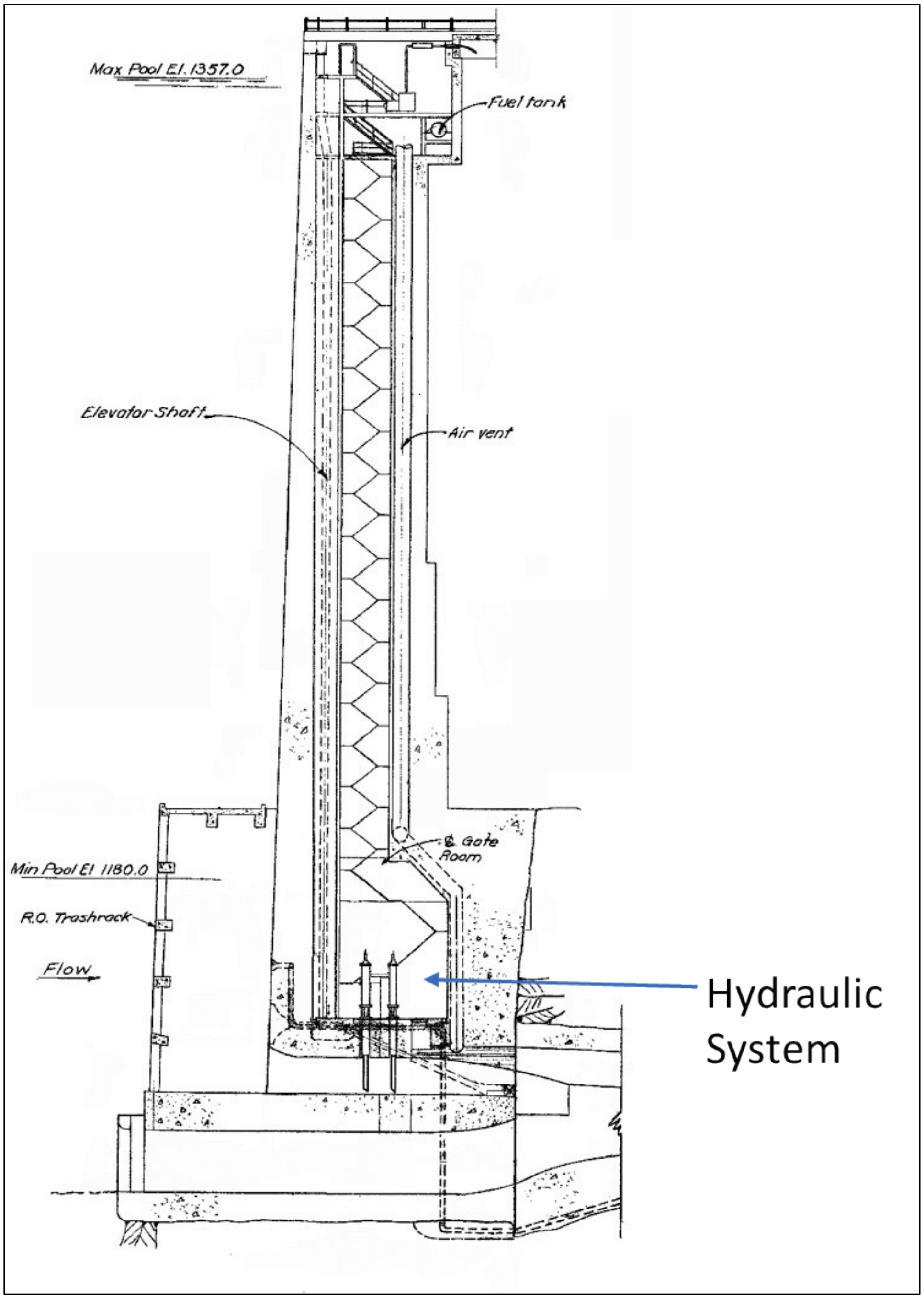
1.3.3 Hills Creek Dam

Hills Creek Dam was constructed in 1961 and is primarily a flood control and water storage facility, although it does have hydropower generation. Hills Creek has a similar, but older hydraulic system. Because the dam is older, it uses a different hydraulic oil (Chevron Hydraulic Oil AW) than the Blue River and Cougar Dams. The Chevron Hydraulic Oil AW does not contain the ZDDP additive (see section 1.9.4).

1.4 Intake tower

Intake towers are vertical structures in reservoirs that routinely convey water as part of the reservoirs operation. For many reservoirs, intake towers provide water for hydroelectric turbines or for water treatment for potable uses. In the case of the Blue River Dam, the intake tower is used to regulate routine releases as part of its mission for flood risk management, recreation, irrigation, and maintenance water quality in the Willamette Valley. Figure 3 is a schematic of Blue River Dam's intake tower. The purpose of the intake tower hydraulic system is to control valves that regulate water levels in the dam.

Figure 3. Schematic of the intake tower (adapted from Crocker 2016).



1.5 Hydraulic system

Figure 4 is a schematic of the hydraulic system showing service gates, control unit, sump, and filters. Figure 5 includes schematics of the control unit. Figure 6 shows the control unit with key sample locations including the tank heater. The tank heater is a Chromalox brand electric immersion heater (2kW, 15 W/in^2, set to 80 °F), model number ARMTO-2020 E1T1.

The tank heater maintains the hydraulic oil at an ideal temperature so that it is at the correct operating viscosity at all times (reducing system pressures and stresses) as well as maintaining a temperature to prevent condensation inside the Hydraulic Power Unit (HPU) reservoir (preventing water intrusion). Temperature gauges record the oil temperature in the sump to insure it does not get too hot (Figure 7). In addition, the hydraulic system has a filtration system to keep the oil free of particulates (Figure 8). Locations of these Figures can be related to the sample locations discussed in the Materials and Methods Section. The system can adjust to changes of pressure using breathers. Reservoir size is 225 gallons, 36 in. W x 72 in. L x 23.5 in. H; the typical volume is 150–200 gallons. The breathers are a desiccant style breather (Hydac Brand with Beta 3 = 200).

Figure 4. Schematic of the Blue River Dam regulating outlet hydraulic system.

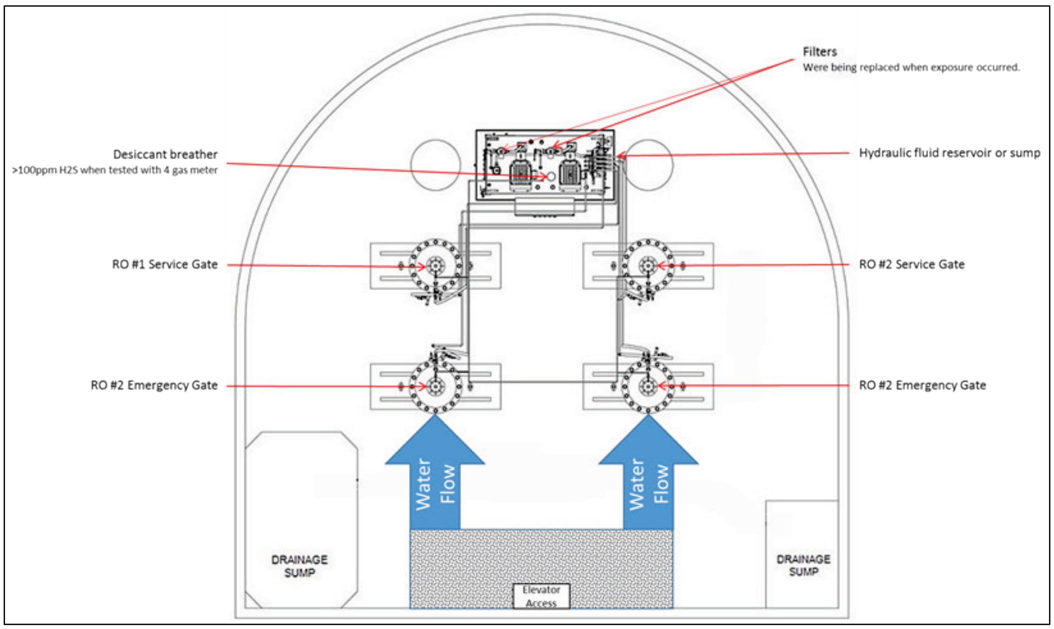


Figure 5. Schematic of the Blue River Dam hydraulic system.

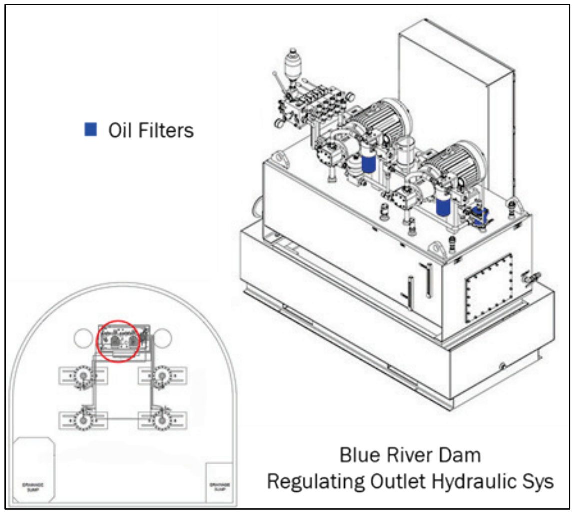


Figure 6. Labelled photograph of the hydraulic fluid system showing key sampling locations.

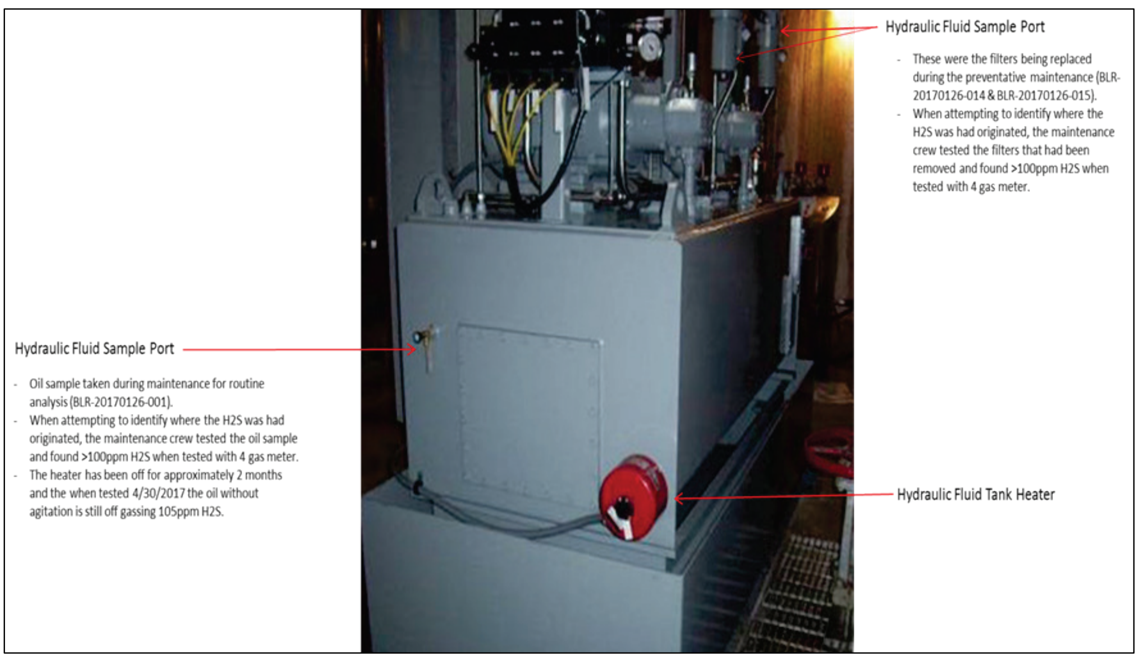


Figure 7. Blue River hydraulic system oil sump temperature gauge.

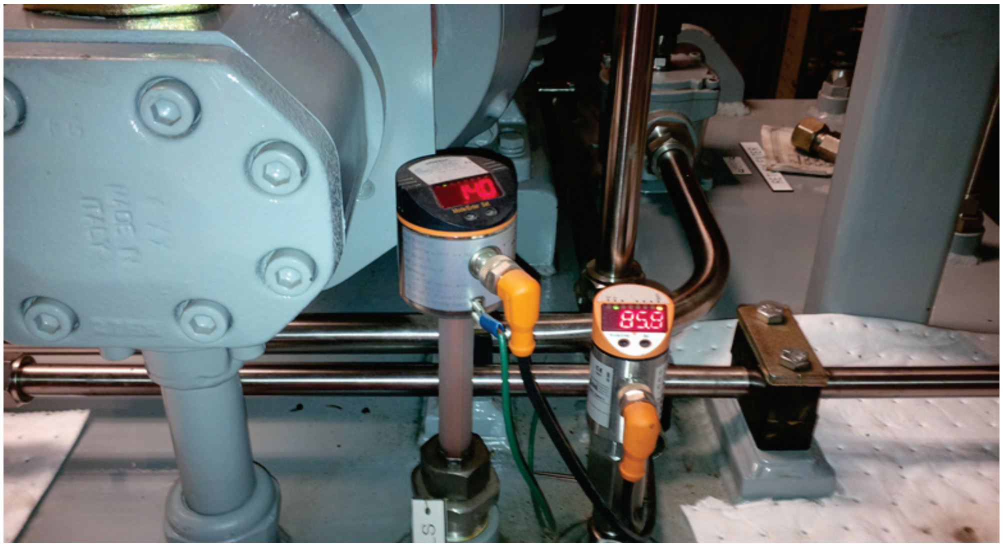
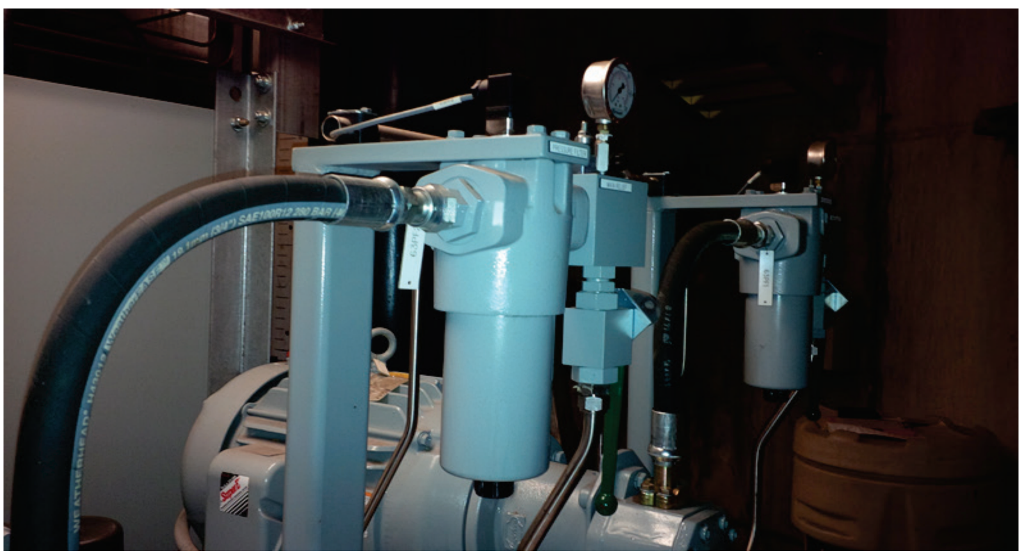


Figure 8. Blue River hydraulic oil system return filter housing.



1.6 Description of the event

Information on the sulfide release event that occurred in October 2016, was obtained through a review of two sources; the summary document (prepared by Catherine Campbell), USACE NWP (Appendix 1), and from a presentation (Crocker 2016). During maintenance in the room containing the hydraulic system, four workers (of a team of five) were affected by hydrogen sulfide gas. A brief rotten egg odor was reported. Interviews conducted by the Board of Inquiry (BOI) indicated that the Project personnel were most strongly affected by the H_2S when the pump motor blowers were blowing air from the sump breather into their faces. Reported symptoms were correlated with distance from the sump tank (Table 2).

Table 2. Distance from hydraulic oil sump tank vs. symptoms (adapted from Crocker 2016).

Symptom	Distance from Hydraulic Oil Sump Tank				
	<1 ft	2 ft	3 ft	10 ft	<10ft
Nose irritation	X	X	X		
Eye irritation	X	X	X		
Throat irritation	X		X		
Headache	X	X	X	X	
Fatigue	X	X			
Disorientation	X				
Memory loss	X				
Tightening in chest	X	X	X		
Coughing	X		X		
Difficulty breathing	X				

An H_2S meter was used to assess the sulfide gas in the hydraulic room. The oil sample and the breather on the sump tank caused the H_2S meter to deflect to its maximum of 100 ppmv (15 ppmv is the Short Term Exposure Limit [STEL] for H_2S). However, H_2S did not register on the meter anywhere else in the tower. All of these observations suggest that the hydraulic oil was the primary source of the H_2S gas.

1.7 Sulfide in oil

Sulfur is commonly found in petroleum, usually organic in form, as impurities to various hydrocarbon compounds that make up the oil. Different crude oil sources have different amounts of sulfur in their composition. Those with total sulfur concentrations of 0.5% (5000 mg/kg) are considered to have high sulfur concentrations and are referred to as sour. Crude oil with sulfur concentrations <0.42% are considered low in sulfur and are referred to as sweet. In crude oil reservoirs, conversion of elemental and organic sulfur to sulfate, then sulfide, is common. The high organic environment creates an ideal environment for reductive microbial reactions and abiotic thermochemical reductive reactions that result in the formation of hydrogen sulfide (Marriott et al. 2015). Modern production methods, including steam assisted gravity drainage and hydraulic fracturing, can actually stimulate sulfide transformation in the production process. Additional chemical additives used in production can add sulfur to the system (Lipus et al. 2017).

However, refined products have sulfur concentrations that are much lower. First, there are many crude sources that have low sulfur content (referred to as sweet). Second, refining processes allow for sulfur removal from sour sources. That said, even after refining, it is common for oils to have sulfur concentrations containing 10s of mg/kg. Additives, however, (such as ZDDP, section 1.9.4) can increase the sulfur content.

As long as this sulfur remains in an elemental or organic form, it does not represent a hazard. However, if it is converted to sulfide, then the oil becomes a source of hydrogen sulfide gas. According to Nicholson and O'Brien (2001), 1 mg/kg of H_2S in oil can result in a vapor concentration of 50 ppmv, this is above the PEL and equivalent to the 10-minute exposure peak (Table 1).

1.8 Hydraulic systems

Many locks and dams are now using hydraulic power systems to operate gates and valves, essentially replacing mechanical drive systems. These systems offer major advantages over mechanical devises like pulleys, levers and gears such as the following:

1. High power to size ratio,
2. Forces can be transmitted over a great distance,
3. Allows large loads to be moved by small forces,
4. Almost infinite speed and forces, speed can be adjusted to meet varying requirements,
5. Can serve many actuators/applications at one time, and
6. Fluid does not break, however, it can become contaminated. Keeping hydraulic fluid clean and dry is critical for proper operation of hydraulic power systems.

1.9 Hydraulic oil

Hydraulic systems rely on fluid or oil pressure to operate. In order to maintain operating pressure, hydraulic oil should be "stiff," (have a high bulk modulus for position stability), should be free of air and water to the best extent possible, and have the ability to transfer heat. Hydraulic oil (when conditioned) flow can carry "cool oil" to cool a heat sensitive component, or, "carry-off heat" away from a component that's oil is exposed to a high temperature.

One of the most important elements of any hydraulic system is the type and quality of the oil. Frequent maintenance of the oil is essential for maintaining high performance operation, equipment reliability, and component life. Hydraulic Oil is assigned International Organization for Standardization (ISO) viscosity grades (VG) ranging from 32 to 68.

An appropriate hydraulic oil should protect against wear of the hydraulic system components. This may involve the use of additive packages to enhance this property. Systems in dams and locks frequently have long pipe runs that can have high variation in temperature. An oil should have proper viscosity to maintain sealing and lubrication in such a setting. Corrosion protection is important, and additives are frequently used to enhance this property. The oil must also be compatible with seals and hoses in the system.

There are three-categories of oil commonly used: 1) petroleum based fluids, 2) biodegradable (or environmentally acceptable), and 3) fire resistant fluids. The three dams in this study all use petroleum based hydraulic oils.

1.9.1 Additives

Hydraulic oils frequently contain additives that serve the following three purposes:

- Modify the properties of the base fluid - improve viscosity index (VI), lower pour point, and reduce foaming,
- Protect the lubricant- slow down oxidation, and
- Protect the equipment - reduce corrosion and protect against wear.

Temperature can affect hydraulic oil performance. If the oil is too cold, any moisture in the oil can precipitate, hydrolyzing the oil. However, if oil is too hot, seals can become damaged, acids can form in the oil, and sludge and varnish can form, all of these can damage the performance of the oil.

1.9.2 Water in hydraulic oil

Water is common in hydraulic oil systems in dams, particularly those that control submerged valves and gates. The systems are under high pressure and it is difficult to insure that seals and pipe joints are completely water tight. Water can seep into the system in this manner. Water can also enter the reservoir through breathers. As outside air is heated up during the day and cooled at night, water can condense out.

Water can exist as free water (a separate phase), dissolved (small quantities [up to 200 to 300 mg/kg] dissolved in the oil), or emulsified (a pseudo-stable oil/water mixture creating a milky mixture, water composing up to 1%). The saturation point is the highest level water can dissolve into a given oil. If the saturation point is exceeded, water will form a free phase.

However, water in the system is not desirable (Kopecky 2004). Water can lead to oil degradation, corrosion, wear, and poor lubrication. Water can also stimulate microbial activity. Microorganisms can degrade the oil, causing biofilms that result in fouling. Water can also react with additives in the fluid. Of particular concern is reaction with ZDDP (Kopecky 2004), this is discussed in section 1.9.4. Although it is ideal that water content be completely eliminated, this is not always practical. However, 200 mg/kg is considered the threshold where the negative effects of water are minimized (Kopecky 2004).

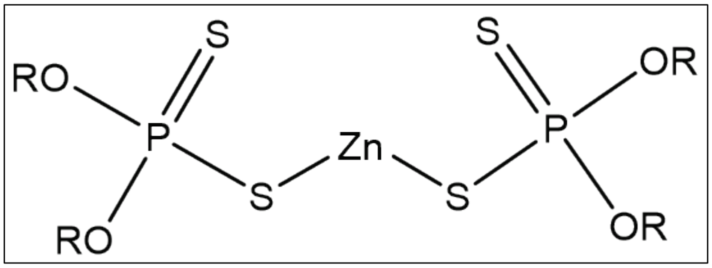
1.9.3 Rando® oil

Both Blue River Dam and Cougar Dam use Chevron Rando® HD hydraulic oil in their systems. This is a premium, petroleum based hydraulic oil designed to work in challenging environments. The oil contains anti-wear additives to minimize wear, contains rust inhibition packages, and is designed to be easily filtered in the presence of water. It resists foaming and has good gas release properties. Appendix 2 contains a product description sheet and a material safety data sheet (MSDS) for Chevron Rando® HD.

1.9.4 ZDDP additive

ZDDP is a common additive to lubrication and hydraulic oils. The purpose of this additive is to reduce wear when it is blended with oil products in concentrations of up to 30% ([American Chemistry Council] ACC 2015). Figure 9 shows a generalized chemical structure for ZDDP. The form in the Chevron Rando Oil® is identified by Chemical Abstract Services (CAS) 68649-42-3, this has a chemical formula of $C_{28}H_{60}O_4P_2S_4Zn$.

Figure 9. Chemical structure of ZDDP.



ZDDP can thermally decompose and form H_2S (ACC 2015). Other gases can also be formed included mercaptans and olefins. ZDDP can also hydrolyze with water to release hydrogen sulfide and sulfuric acid (Kopecky 2004; ACC 2015). A proposed balanced equation for this reaction is

$C_{28}H_{60}O_4P_2S_4Zn + 60\ H_2O = 8\ Zn + 27\ H_2S + 5\ H_2SO_4 + 16\ H_3PO_4 + 8\ C_{28}H_{60}OH$ (Equation balanced by Mr. Justin La)

The reaction is catalyzed by higher temperatures.

2 Materials and Methods

2.1 Quality assurance plan (QAP)

ERDC prepared a quality assurance plan (QAP) for the study, this is provided in Appendix 3.

2.2 Samples

Samples from three dams (Blue River Dam, Cougar Dam, and Hills Creek Dam) were collected by NWP (Figure 10). The total number of samples were seventeen hydraulic oil samples (Table 3) and four water samples (two from Blue River Dam, and one each from Cougar Dam and Hills Creek Dam). Two of the samples were "new" oil, meaning that they were unused Chevron Rando oil. The ERDC also received two filter samples from the Blue River Dam.

Figure 10. Samples collected for the study.

Table 3. Hydraulic oil samples collected for this study.

Sample Number	Date	Sample Location
Blue River		
1	10/18/2016	Original Oil
2	1/28/2017	HPU oil sump tank sample port
3	1/28/2017	HPU oil sump tank drain port
4	1/28/2017	RO #1 Service Port
5	1/28/2017	RO #1 Service Bottom
6	1/28/2017	RO #1 Emergency Top
7	1/28/2017	RO #1 Emergency Bottom
8	1/28/2017	RO #2 Service Top
9	1/28/2017	RO #2 Service Bottom
10	1/28/2017	RO #2 Emergency Top
11	1/28/2017	RO #2 Emergency Bottom
16	1/28/2017	Chevron Rando HD-ISO-32 NEW Oil
17	1/28/2017	Chevron Rando HD-ISO-32 NEW Oil
Cougar Dam		
1	1/28/2017	HPU oil sump tank sample port
2	1/28/2017	HPU oil sump tank drain port
Hills Creek Dam		
1	1/28/2017	HPU oil sump tank sample port
2	1/28/2017	HPU oil sump tank drain port

The following water samples were collected:

- Blue River Dam (BLR)-12 – drainage sump. 01/28/2017.
- BLR-13 – reservoir near intake tower. 01/28/2017.
- Cougar Dam (CGR)-3 – reservoir near intake tower. 01/28/2017.
- Hills Creek Dam (HCR)-3 – reservoir near intake tower. 01/28/2017.

2.2.1 Oil sample studies

Oil samples were studied for the analytes specified in Table 4. Contract laboratories were used for these analyses as indicated. These analyses were conducted by Air, Water & Soil Laboratories, Inc. (Richmond, VA).

Table 4. Analytes for hydraulic oil samples collected for sulfide study.

Analyte	Method	Detection Limit
Water Content	American Society for Testing and Materials (ASTM) D95	10 mg/kg (estimated)
Acid Neutralization Number	ASTM D664	Up to 0.01 mg/kg
Zinc	USEPA Method 6010C (SW-846)	0.5 mg/kg
Sulfur	USEPA Method 6010B (SW-846)	8.33 mg/kg

Water content, zinc, sulfur, and acid numbers were analyzed by a contract laboratory. Sulfur reducing microorganisms were analyzed at ERDC.

2.2.2 Water samples

Water samples were measured for the analytes specified in Table 5. The analyses were conducted by the Environmental Chemistry Branch (EPC) of ERDC (Vicksburg, MS) using the United States Environmental Protection Agency (USEPA) method listed.

Table 5. Analytes for water samples collected for sulfide study.

Analyte	Method	Detection Limit
pH	USEPA Method 150.1	0.01 units
Specific conductance	USEPA Method 120.1	1 uS/cm
Sulfate	USEPA Method 9035 (SW-846)	0.004 mg/L
Sulfide	USEPA Method 376.2	0.01 mg/L
Zinc	USEPA Method 6020 (SW-846)	0.002 mg/L
Sulfur	USEPA Method 6010 (SW-846)	mg/L

2.2.3 Hydraulic filters

The ERDC received two hydraulic oil filter samples from Blue River Dam. The oil filters were Hydac brand filters, model 0240D005BN4HC (5 micron, Beta 5 = 1000). These filters were taken apart and separated into different components that were then studied at 8–100X magnification using a Leica MX12.5 Stereo microscope (https://www.meyerinst.com/html/leica/mz125/mz125.htm). Pictures were taken to document the results.

2.2.4 Sulfur reducing microorganisms

The study included seventeen hydraulic oil and water samples from the three dams. Appendix 4 contains the report on this portion of the study, and it discusses the methods in detail. In summary, genetic probes were used to search for microbial activity and sulfur reducing microorganisms in both oil and water samples. Samples were explored using the two following primers:

- The first searched for bacterial DNA (deoxyribonucleic acid),
- If the first was positive, then the second searched for genetic material associated with sulfate reducing bacteria.

3 Results

3.1 Chemical analyses

3.1.1 Hydraulic oil

Table 6 summarizes the analytical data for the hydraulic oil samples. Subsequent sections will refer back to these results.

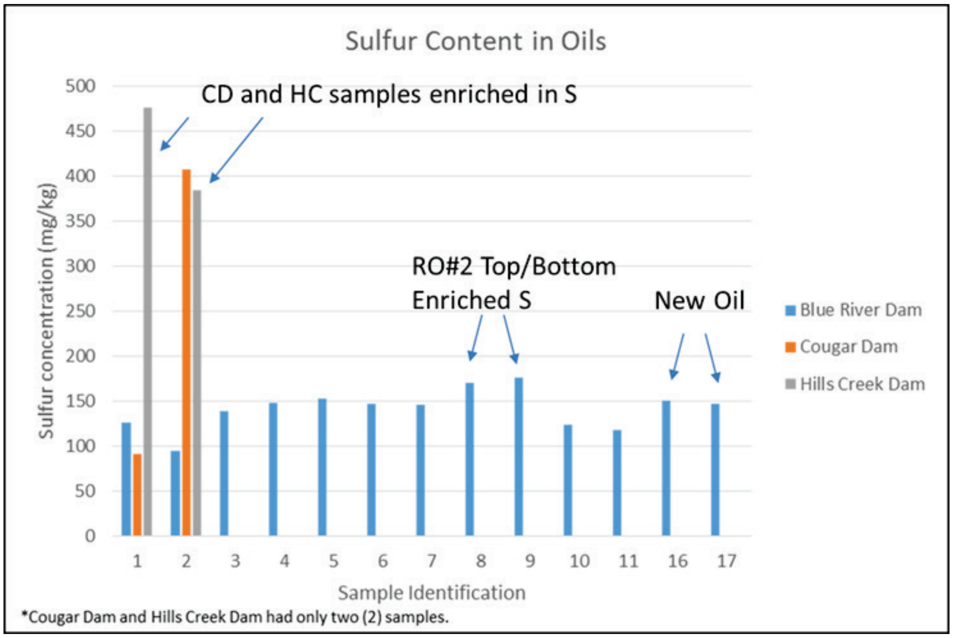
Table 6. Summary of results of hydraulic oil analyses.

Sample ID	Acid Neutralization (mgKOH/g)	Water, % (wt%)	Zinc (mg/kg)	Sulfur (mg/kg)
Method	ASTM D664	ASTM D6304	EPA 6000/7000	Digestion: SW-846 3050B. Analysis by ICPMS SW-846 6010B
Blue River Dam				
BLR-20170126-001	0.14	0.051	180	126
BLR-20170126-002	0.25	0.028	162	94.7
BLR-20170126-003	0.23	0.015	166	139
BLR-20170126-004	0.23	0.017	157	148
BLR-20170126-005	0.14	0.012	161	152
BLR-20170126-006	0.29	0.016	232	147
BLR-20170126-007	0.29	0.015	270	145
BLR-20170126-008	0.28	0.092	224	170
BLR-20170126-009	0.48	0.077	197	176
BLR-20170126-010	0.27	0.024	206	124
BLR-20170126-011	0.24	0.029	209	118
BLR-20170126-016	0.25	0.021	420	150
BLR-20170126-017	0.32	0.013	401	147
Cougar Dam				
CGR-20170126-001	0.21	0.169	380	90.8
CGR-20170126-002	0.27	0.056	392	407
Hills Creek Dam				
HCR-20170126-001	0.03	3.35		476
HCR-20170126-002	0.11	44.8	BLD	384

3.1.1.1 Total sulfur in hydraulic oil

Figure 11 summarizes the total sulfur in the hydraulic oil samples. All of the oil samples had sulfur contents of at least 90.8 mg/kg. This indicates that there is sufficient sulfur in the oil samples to serve as a source of hydrogen sulfide. Blue River Dam samples sulfur content ranged from 94.7 to 170 mg/kg. Fresh oil samples (Blue River Dam 16 and 17) had sulfur levels of approximately 150 mg/kg (147 and 150 respectively). Samples 4, 5, 6, and 7 had levels ranging from 145 to 152 mg/kg, or approximately the same as that of the base oil. Samples 8 and 9 (RO#2 Top and Bottom respectively) had sulfur concentrations of 170 to 176, or slightly enhanced sulfur content. Conversely, samples 1, 2, 3, 10 and 11 had sulfur levels lower than that of the base oil (94.7 to 139 mg/kg).

Figure 11. Total sulfur in hydraulic oil samples.



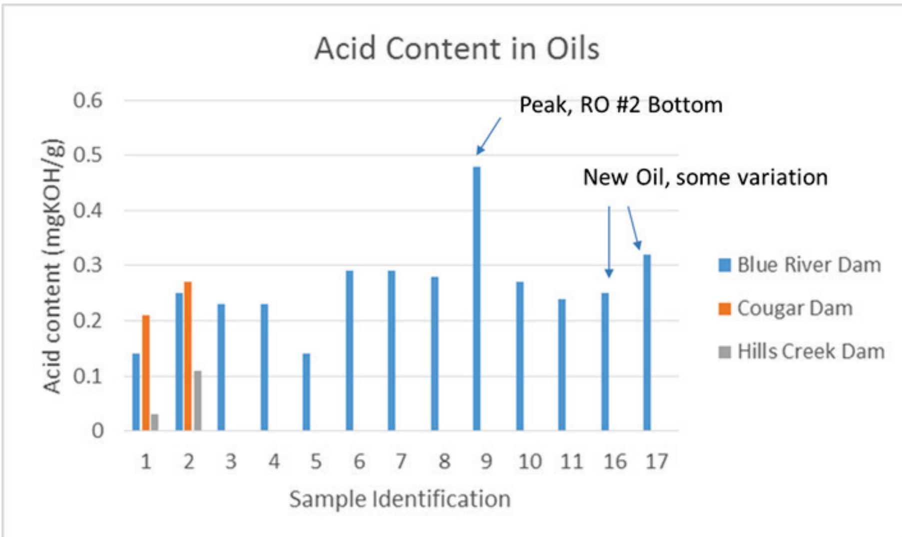
Comparing oil samples to those of the other dams provides some interesting results. Sulfur samples for the oil at Hills Creek Dam were as high as 476 mg/kg, substantially higher than sulfur samples in Blue River samples. Hills Creek does use a different hydraulic oil compared to Blue River and Cougar Dams. Cougar Dam, on the other hand, also used Rando® HD oil. Sample 1 (oil sump tank sample port) had the most depleted sulfur level (90.8 mg/kg). However, sample 2 (oil sump tank drain port) had a very high sulfur level of 407 mg/kg.

3.1.1.2 Acid neutralization number

Figure 12 summarizes the acid neutralization numbers in hydraulic oil samples. The acid neutralization number is used as a measurement of how the oil is aging and oxidizing. Blue River Dam samples acid content ranged from 0.14 to 0.48 mgKOH/g. The new oil (samples 16 and 17) had neutralization numbers of 0.25 and 0.32 mgKOH/g respectively, nearly a 30% variation. Therefore, it appears that this measurement does have some inherent variation. Samples 2, 6, 7, 8, 10, and 11 had concentrations ranging from 0.24 to 0.29 mgKOH/g, close to the range of the new oil samples. Samples 3 and 4 were slightly decreased in acid neutralization, both with measurements of 0.23 mgKOH/g. Samples 1 and 4 had more substantial decreases in acid neutralization measurements, both with measurements of 0.14 mgKOH/g. Sample 9 had a highly elevated acid neutralization number of 0.48 mgKOH/g.

Comparing sample locations 1 and 2 of Blue River Dam acid neutralization numbers to Cougar Dam, indicate the Blue River Dam numbers were slightly less, but samples from both dams had similar concentrations. Both Cougar and Blue River Dams neutralization numbers were higher than those at Hills Creek Dam (note that Hills Creek Dam does use a different hydraulic oil).

Figure 12. Acid neutralization numbers in hydraulic oil samples.



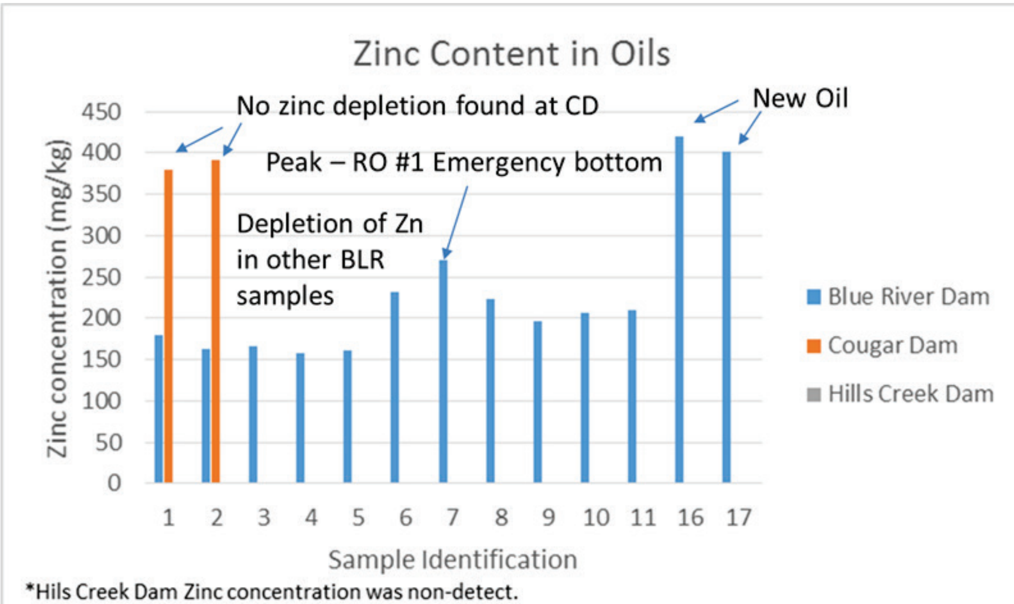
Interestingly, the acid neutralization numbers measured in the study were all high. 0.15 mg KOH/g is considered a normal level for most new oils, 0.20 mg KOH/g is a warning level that the oil is getting too acidic and 0.30 mg KOH/g is a critical warning. However, the new oil samples exceeded the warning level and one actually exceeded the critical level. Most of the samples were higher than 0.2 mg KOH/g, the warning level.

3.1.1.3 Zinc concentration

Zinc concentrations in Blue River Dam samples ranged from 157 to 420 mg/kg (Figure 13). The highest concentrations were found in the new oil samples (401 and 420 mg/kg). The oil samples collected from the Blue River Dam hydraulic system were all depleted in zinc, with concentrations ranging from 157 to 270 mg/kg. Of the Blue River Dam samples, the highest concentration was found at sample 7, the RO #1 Emergency bottom.

The Blue River Dam concentrations for sample points 1 and 2 were less than half of those found at Cougar Dam at the same sample points. The Cougar Dam concentrations were comparable to those for the new oil, indicating that zinc depletion had not occurred. Hills Creek Dam samples were non-detect (note the Hill Creek Dam hydraulic system uses a different oil that does not contain ZDDP).

Figure 13. Zinc concentration in hydraulic oils in this study.

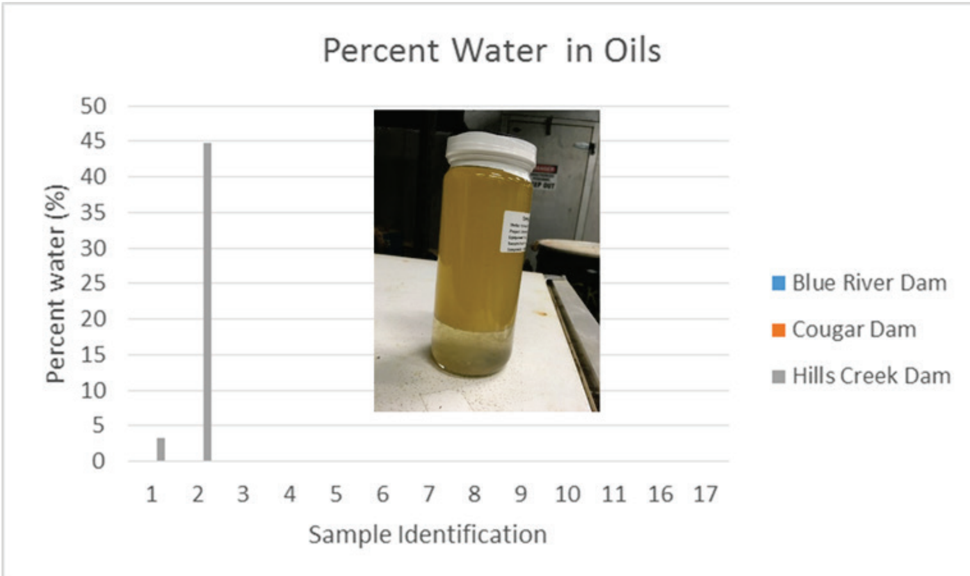


3.1.1.4 Percent water in hydraulic oils

Figure 14 summarizes percent water found in the oil samples collected for this study. The results were heavily skewed by water in the Hills Creek Dam oil samples, these were as high as 45% (as a side note, this level is extremely high and an investigation is recommended). The picture inset (Figure 14) shows that the water was clearly visible in the oil sample.

The new oil samples had water concentrations of 0.013 and 0.021%. Blue River Dam samples ranged from 0.012 to 0.077%. Water concentrations in the two Cougar Lake Dam samples were 0.056 and 0.169%.

Figure 14. Percent water in oil samples in the study. The high concentrations in the Hills Creek Dam oil samples dominate the graph. The photo inset shows a separate water phase in one of the Hills Creek Dam samples.



Generally, water content in oils should be kept below 250 ppm, or 0.025%. Obviously, something very wrong had occurred with the Hills Creek Dam oil samples and they far exceeded this value. Both samples at Cougar Dam also exceeded the threshold (Table 6). At Blue River Dam, four of the thirteen measured samples exceeded this threshold (Table 6).

3.1.1.5 Graphs exploring relationships between the oil parameters

Figures 15–17 are graphs prepared to explore relationships of water, zinc, and acid number with sulfur in the oil samples. Unfortunately, the data does not lend itself to statistical tests (e.g., t-test or ANOVA) that are focused on determining if a difference between two populations is statistically significant. In this case, graphed data explores if a linear, exponential, or logarithmic relationship between the parameters shows regression, this is an acceptable statistical test. Hills Creek Dam data is included in the graphs (except for the one exploring water content and even though it was a different oil type) so as to increase the total data points in an effort to see a pattern. Unfortunately, no such relations were evident.

Figure 15. Relationship of percent water and sulfur. (Note, Hill Creek Dam data is not included in the graph because it skewed the graph, but it also did not show an obvious relationship).

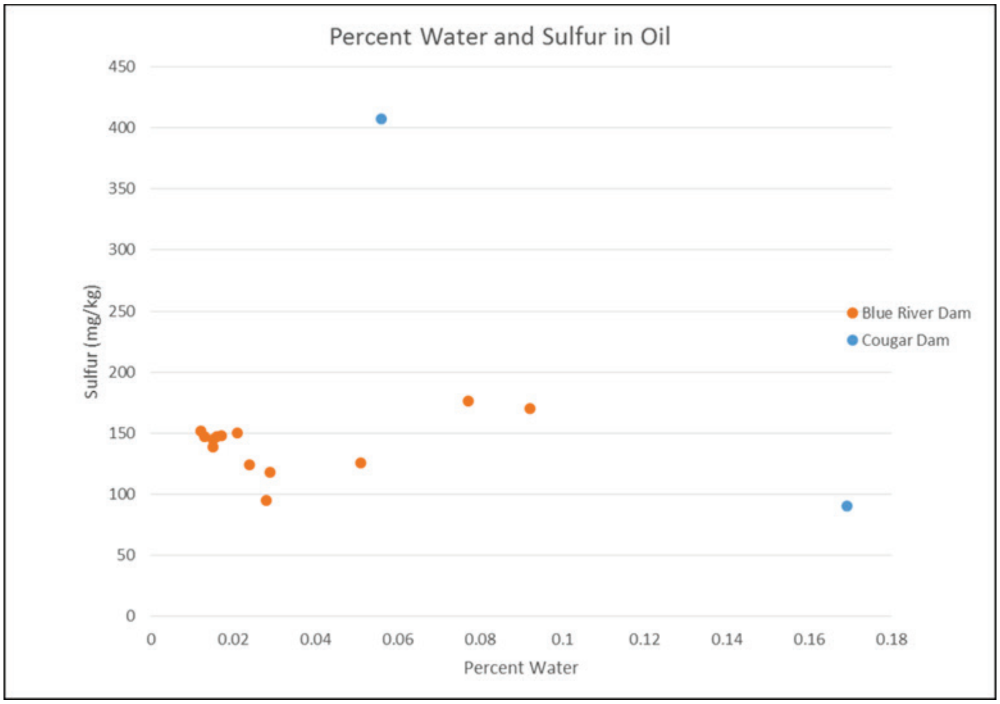


Figure 16. Relationship of zinc concentration and sulfur.

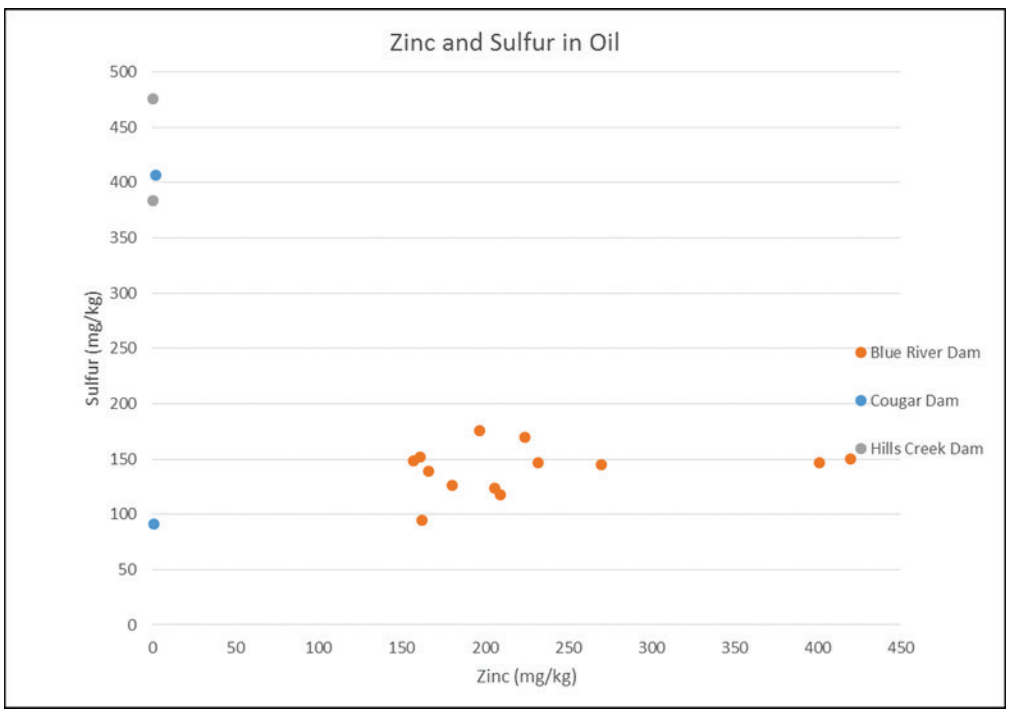
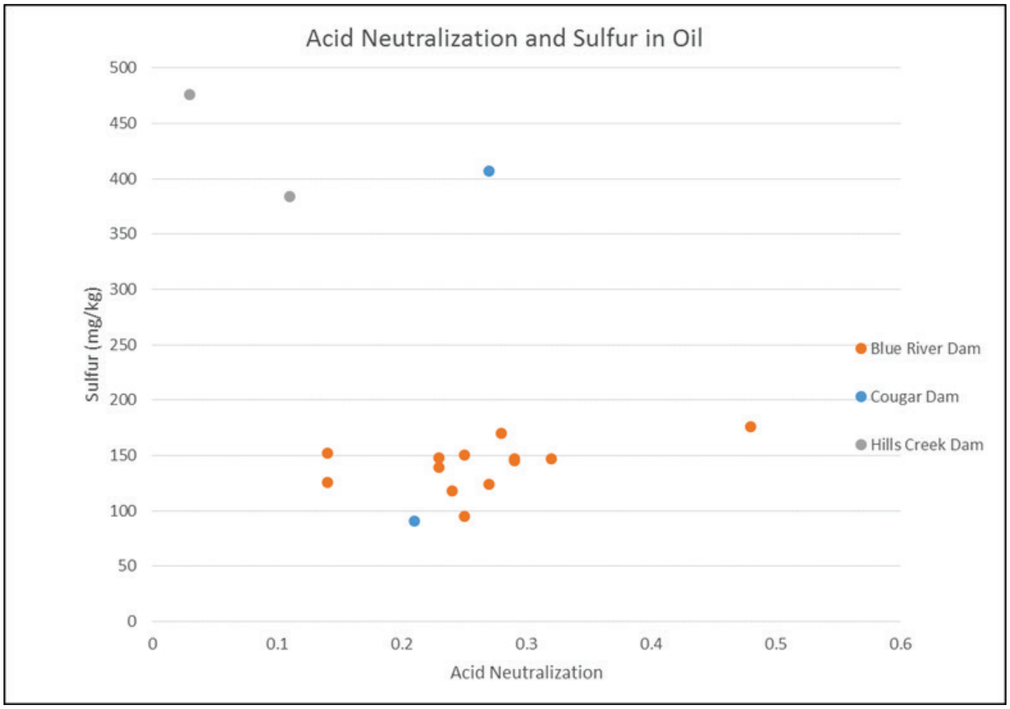


Figure 17. Relationship of acid neutralization number and sulfur.



3.1.2 Water samples

3.1.2.1 Chemical measurements in water samples

Table 7 summarizes water chemistry from samples collected in the Blue River Dam hydraulic system drainage sump (sample 012) and from the Blue River Dam reservoir (sample 013). Reservoir samples were collected from Cougar Dam (003) and Hills Creek Dam (003). In comparing the reservoir samples, the pH of the three samples were relatively close, ranging from 7.33 to 7.60. Conductivity measurements had a greater range, with the Blue River Dam sample having the lowest measurement of 30.6 S/m and the Hills Creek Dam sample having the highest number of 47.0 S/m.

The Blue River Dam sump sample had the highest zinc concentration measured at 0.0133 mg/kg. This was higher than zinc levels in the Cougar Dam and Hills Creek Dam sumps (0.0057 and 0.0094 mg/kg). The Blue River Dam samples had higher sulfate and sulfur concentrations, however, sulfide was found in Cougar Dam and Hills Creek Dam, but not in Blue River Dam (see section 3.1.2.2 for a more detailed analysis of sulfur measurements).

The Blue River Dam sump water was higher in pH (9.82 vs. 7.60) and conductivity (118 vs. 30.6 S/m) compared to the water sample from the Blue River Reservoir. The sump water also had higher sulfate and total sulfur concentrations.

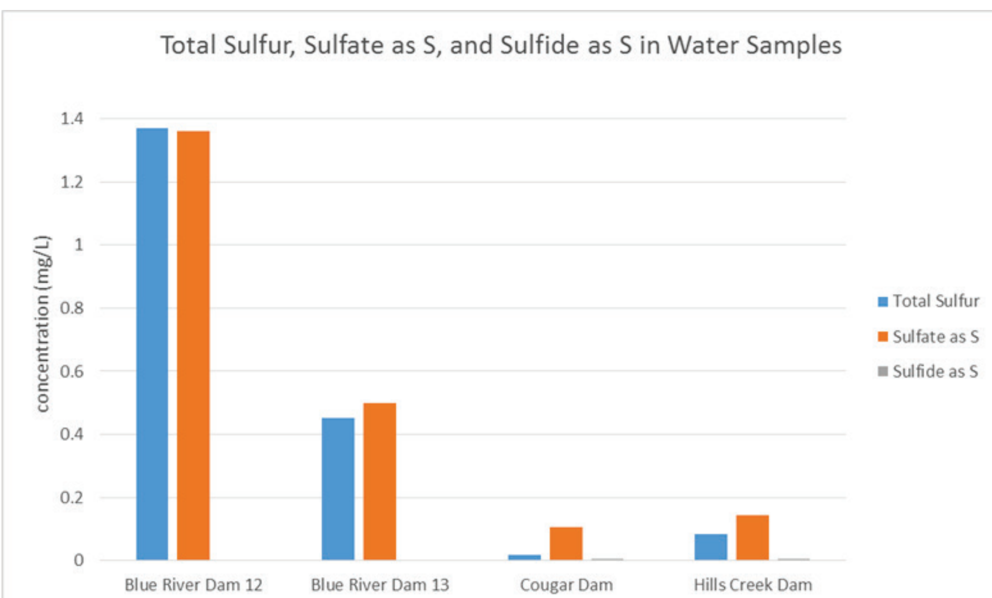
Table 7. Analytical data for water samples.

Sample ID	Conductivity (S/m)	pH	Sulfate (mg/L)	Sulfide (mg/L)	Sulfur (mg/L)	Zinc (mg/L)
Method	EPA 120.1	EPA 150.1	EPA 300.0	EPA 376	SW 846/6010	SW 846/6010
Blue River Dam						
BLR-20170126-012	118	9.82	4.08	ND	1.37	0.0133
BLR-20170126-013	30.6	7.60	1.50	ND	0.452	0.0080
Cougar Dam						
CGR-20170126-003	38.2	7.33	0.316	0.0102	0.0189	0.0057
Hills Creek Dam						
HCR-20170126-003	47.0	7.37	0.426	0.0114	0.0825	0.0094

3.1.2.2 Sulfur species

Sulfate and sulfide were adjusted as mg/L as S to allow direct comparison with total sulfur (Figure 18). Water samples collected from the Blue River Dam site were substantially higher in total sulfur concentrations than those collected from Cougar Dam and Hills Creek Dam. This might be a factor in the sulfide emissions found at Blue River Dam. Sulfur was mostly in the form of sulfate. Some sulfide was found at Cougar Dam and Hills Creek Dam, but not in the Blue River Dam samples.

Figure 18. Comparison of sulfur species in water samples.



3.2 Filter study

3.2.1 Received filters

The ERDC received two filters:

- Blue River 014
- Blue River 015

Both were described as *original oil filters*, and both were relatively clean in appearance (Figure 19).

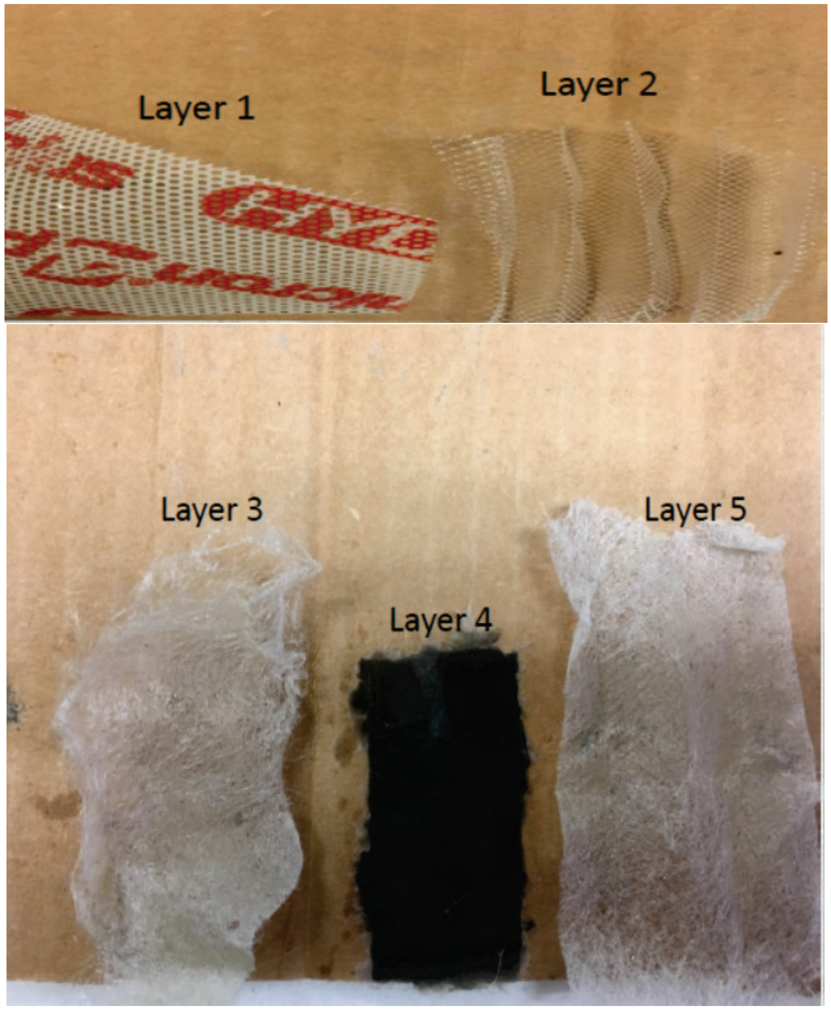
Figure 19. One of the hydraulic oil system filters received for the study.

3.2.2 Filter components

The filters consisted of five layers (Figure 20):

1. Outer section of large holes in metal housing.
2. A plastic wire mesh.
3. A denser mesh material.
4. A still more dense mesh material.
5. A final material similar in density to layer 3.

Figure 20. The five materials found in the hydraulic oil filter.



3.2.3 Observations

The materials were studied at magnifications ranging from 8 to 100X. Results from filter 014 are shown in Figures 21–25. No evidence of biofilm was observed. Although not shown, observations of filter 015 were identical to those of 014.

Figure 21. Magnified view of Layer 1 (8X). No evidence of biological growth.

Figure 22. Magnified view of layer 2 (25X). No evidence of biological growth.

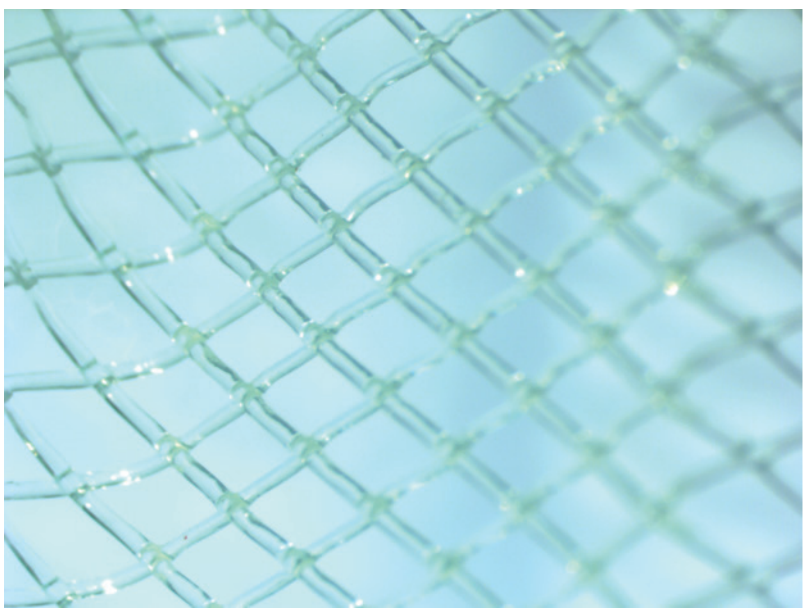


Figure 23. Magnified view of Layer 3 (50X). No evidence of biological growth.

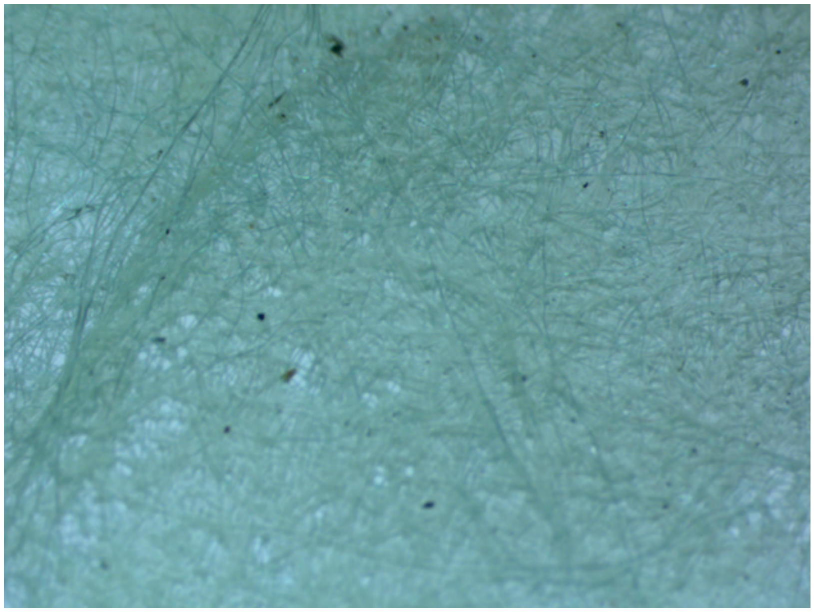


Figure 24. Magnified view of Layer 4 (100X) No evidence of biological growth.

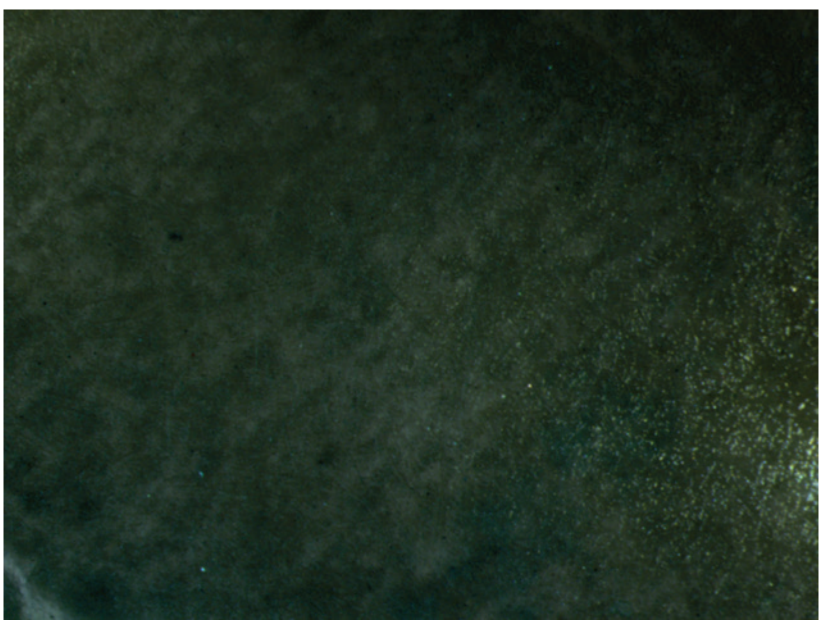
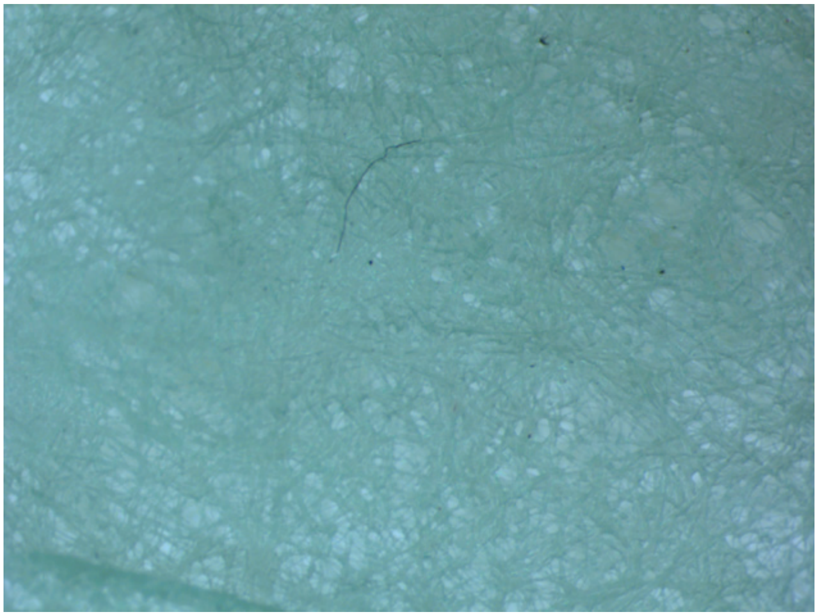


Figure 25. Magnified view of Layer 5 (50X). No evidence of biological growth.



3.3 Genetic probing of hydraulic oil and water samples

A complete report on the genetic probe work is attached in Appendix 4. In summary:

- The study included seventeen hydraulic oil and water samples from the three dams.
- Samples were explored using two primers:
  - The first searched for bacterial DNA.
  - If the first was positive, then the second searched for genetic material associated with sulfate reducing bacteria.
- Only ten samples showed evidence of bacterial DNA:
  - None were found in the *new* oil samples.
  - Positive in water samples for all three dams.
  - Five in seventeen oil samples for the Blue River Dam and Hills Creek Dam oil samples.

No evidence was found of sulfate reducing bacteria in either water or oil samples that were taken.

4 Discussion

4.1 Biological activity

The focus of this study was to investigate if biological activity was responsible for the hydrogen sulfide production in the Blue River Dam hydraulic system. The results suggest that the hypothesis should be rejected. This study found only minimal markers of biological activity in the hydraulic oil, and none indicating sulfur reducing bacteria (SRB). Also, the study found no evidence of biofilms in the oil filters. Future studies should focus on more detailed sampling from the sump areas where the hydrogen sulfide vapors were first found, perhaps including wipe samples of the sump if feasible. Still, no SRBs were found in the sump samples evaluated in this study.

4.2 Hydraulic oil measurements

Even though biological activity was ruled out, studying the hydraulic oil measurements identified some areas of concern and provide data on the possible cause of the sulfide emissions.

4.2.1 Areas of interest

In reviewing the hydraulic oil chemistry data, two locations stand out as consistently having values that differ from the new oil, indicating changes to the oil at those locations. They also tend to differ substantially from concentration found in other sample locations. These are the sump and the regulating outlets.

4.2.1.1 Sump

Samples 1 and 2 were collected at the HPU oil sump sample port. Both of these samples had the lowest sulfur measurements and lower zinc concentrations. Sample 1 also had the lowest acid neutralization concentration. Furthermore, the sump tank did appear to be the source of the sulfide vapors during the release event (see section 1, Introduction).

4.2.1.2 Regulating outlet samples (RO#2, top and bottom)

The RO #2 inlet and outlet samples (numbers 8 and 9) had elevated sulfur levels compared to the base oil (170 mg/kg compared to 150 mg/kg for new oil). In addition, sample 9 had the highest acid neutralization number, higher than the new oil samples.

4.2.2 Zinc

This study found zinc depletion in the oil samples collected from the Blue River Dam hydraulic system. The new oil samples contained zinc concentrations of 401 and 420 mg/kg, while the zinc concentrations in the hydraulic oil system were lower, 157 to 270 mg/kg. Samples collected from the Cougar Dam hydraulic system, which is similar and uses the same Chevron Rando® oil, had zinc concentrations in the sump slightly lower, but similar to, that of the new oil (380 and 392 mg/kg). The zinc concentrations in the sump samples at Blue River Dam were 180 and 162 mg/kg.

These results suggest that zinc is depleted over time in the oil. In the Cougar Dam hydraulic system, this depletion is relatively mild, up to 40 mg/kg. However, in the Blue River Dam samples, it was more severe, up to 260 mg/kg. As discussed, zinc is found in the additive ZDDP that is included in the Chevron Rando® oil used at the Blue River Dam. ZDDP is added to the oil to reduce mechanical wear. It is likely that some of the losses of zinc are due to its deposition on surfaces as part of this process (Kopecky 2004). The relatively small losses in zinc concentration found in the Cougar Dam oil is likely due to zinc deposition.

The higher degree of zinc loss in the Blue River Dam oil suggests that another mechanism may be occurring. Zinc does not degrade nor does it commonly form volatile species. The most likely means of zinc loss in the hydraulic oil is through dissolution in water, particularly in the sump. This study found that the water in the Blue River Dam sump had zinc concentrations about three-times higher than those in the Cougar Dam sump.

If the hypothesis that zinc loss in the Blue River Dam oil is due to dissolution in the sump water, then this might also be a mechanism for hydrogen sulfide production. As discussed above in section 1.9.4, ZDDP can form hydrogen sulfide via hydrolysis reactions and these can be enhanced by elevated temperature. The sump was determined to be an area of concern (see section 1.5). A detailed sampling strategy that would include measurements of oil and water volumes could be conducted to allow a detailed mass balance.

4.3 Treatments/water removal

Supplemental water removal systems could be an effective approach to minimize hydrogen sulfide formation. By removing water from the system, then ZDDP hydrolysis reactions should be eliminated. A common approach is called the kidney loop system. In these systems, the fluid is drawn through a water adsorptive media that pulls water out of the oil (Kopecky 2004). This approach is inexpensive and easy to apply, but it is only useful for removing free and emulsified water – it cannot remove dissolved water. Still, free and emulsified water is usually the bulk of the water in the system.

More complete removal can be obtained using vacuum dehydration. These systems use vacuum pressure and condensation to remove free, emulsified, and dissolved water from the hydraulic oil (Figure 26). These systems can also be modified to incorporate sulfide removal. A vacuum system can draw off gas, then react the gas with an iron bed to trap the sulfide as an iron mineral form.

Some other options for water removal include gravity removal (only for free water) and centrifugal systems (free and some emulsified water removal, but not dissolved). Table 8 summarizes several approaches.

Figure 26. A vacuum dehydration hydraulic oil purification system with sulfide removal (High Purity Northwest Inc., www.highpuritynorthwest.com).

Table 8. Water removal approaches for hydraulic oil (adapted from Kopecky 2004).

Separator	Water Type Removed		
	Free	Emulsified	Dissolved
Gravity	Yes	Minimal	No
Centrifuge	Yes	Some	No
Absorbing elements (Kidney loop)	Yes	Yes	No
Vacuum dehydration	Yes	Yes	Yes

5 Conclusions

Based on this study, the following conclusions can be derived:

5.1 Sulfur measurements for hydraulic oil

- No obvious sulfur differences for different hydraulic oil samples collected at Blue River Dam.
- Cougar Dam and Hills Creek Dam samples actually had much higher sulfur than at Blue River Dam. This might indicate that something is occurring at the Blue River Dam resulting in sulfur depletion in the oil.
- Hills Creek Dam had substantially higher percent water than the other sites.
- No obvious relationship with percent water, zinc, or acid neutralization number in relation to sulfur concentrations.

5.2 Sulfur measurements for water samples

- Blue River Dam has substantially higher sulfate and sulfur than Cougar River Dam and Hills Creek Dam.

5.3 Evidence for microbial activity

- Filter samples were very clean, no evidence of microbial growth.
- Microbial activity is limited in hydraulic oil samples, several showed none.
- No evidence of sulfate reducing bacteria.

5.4 Conclusion

- Sulfide production from in the hydraulic oil was most likely abiotic, and most likely due to hydrolysis of ZDDP additive. Also, elevated temperature could play a role.
- Water seepage into the system may be key, providing water for ZDDP reaction.

6 Recommendations

Assuming that a reaction with ZDDP is causing the sulfide release, then the following recommendations are given:

- Focus on Hydrolysis of ZDDP as the most likely cause of H_2S emissions.
- Consider replacing hydraulic oil with one that does not contain ZDDP:
  - Chevron AW® is a hydraulic oil with characteristics that indicate that it can be an effective replacement oil (Catherine Campbell, NWP, Appendix 5 contains the product information sheet).
  - Chevron AW® it is not a seamless replacement. It is not compatible with Chevron Rando®, and would require a service cleanout.
  - Another option would be to identify a suitable Environmentally Acceptable Lubricant (Medina 2015) that reduces issues associated with accident release.
- If it is decided that a ZDDP oil is the best choice, then focus on moisture and temperature control.
  - Take actions to ensure that there are no temperature gradients:
    - Mixing of temperature sampling well.
    - Multiple temperature probes to detect gradients.
  - Water control and sulfide removal:
    - Use of vacuum dehydration or desiccants (kidney loop) to remove water from system.
    - Consider an integrated system that also removes sulfide.
  - Use caution when servicing the system in the future:
    - Follow confined space working procedures.
    - Breathing protection or ventilation.
    - Monitoring equipment for sulfide gas.
  - Consider laboratory studies to explore conditions where hydrolysis reactions occurs:
    - Vary temperature, pressure, water quantity, external sulfur, oil age.
    - Consider a study to conduct a detailed mass balance of zinc in the system.
    - The ERDC can design and execute such a study.

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Appendix A: Project Notes (Provided by Catherine Campbell, NWP)

COMMENTS WELCOME!!! I used Track Changes in minutes below to show changes due to today's discussion.

WE EXPECT TO BE ALLOWED TO FINISH LAB TESTING BEFORE FINALIZING BOI

We know the H2S is in the oil, because the oil sample, and the breather on the sump tank [See "Isometric and Photos.pdf"], peg the H2S meter at 100 ppm. Could not get H2S to register on the meter anywhere else in the tower. Also, interviews led us to believe the Project personnel were most strongly affected when the pump motor blowers were blowing air from the sump breather into their faces.

What caused the H2S?

It could have been the oil itself: Hydraulic oils have widely varying amounts of sulfur, depending on API grade. Grade I can have up to 8000 PPM, but grades II and III have less than 10 PPM. The sulfur is released as H2S when water contamination reacts with the sulfur compounds. Solubility of H2S in oil is "low" but not zero, actual quantified solubility is highly dependent on temperature and Henry's Law constant in relation to the specific hydraulic oil.

It could have been the reservoir water: Sulfur-reducing bacteria, which use sulfur as an energy source, are the primary producers of large quantities of hydrogen sulfide. These bacteria chemically change natural sulfates in water to hydrogen sulfide. Sulfur-reducing bacteria live in oxygen-deficient environments such as deep reservoirs. It is formed from decomposing underground deposits of organic matter such as decaying plant material, and may flourish with heat.

But it was probably the interaction of an additive called ZDDP with water AND/OR WITH HEAT: ZDDP can produce H2S when stored too hot, and though the temperature of the sump at the site visit was about 30 degrees Fahrenheit lower than the long-term heat threshold I found online, the temperature on the surface of the heating element may be above that threshold. This will be looked into further in-house. [See "Safe-Handling-Guidelines-for-ZDDP-Components-and-Blends.pdf"] Hydraulic fluid will typically contain ZDDP (Zinc dialkyldithiophosphate) as an antiwear (and somewhat of an anti-oxidant) additive. I CALLED CHEVRON AND THE "RANDO HD" oil definitely has ZDDP in it. ZDDP content is quite high as an additive, typically ranging from 100 to 1000 ppm. Any compounds with "thio" in the name contain sulfur. Some hydraulic oils are non-zinc in order to protect the copper alloy components. Testing with a lab such as would be needed to verify zinc and sulfur content of new oil identical to that in the system. A spectrochemical analysis would help with that.

ZDDP + Water => H2S + Sulfuric Acid [See "ZDDP Molecule.pdf" and "Kopecky Article.pdf"]

ZDDP is very sensitive to breakdown in the presence of free water. IF water levels are elevated it will break down and H2S is one of the potential byproducts. Water content above 300 ppm is problematic, and anything above 100 ppm should be viewed with suspicion. The recent test results show very low water content [See "Previous Lab Test Results.pdf], but the procedure for drawing a sample for testing is to clean/dry it FIRST, so the test results may not fairly represent the state the oil "dwells" in most of the time. High acid numbers may be an indication that oxidation due to high water content over time has occurred.

But why would HEAT AND/OR water + ZDDP have created this issue ONLY at Blue River? Alan has looked into possible paths for reservoir water to get into the cylinders and it does not look at all likely – it seems the water must have been ambient and entered the sump through the breather. Why not at Cougar, where acid number results are also high? Why not at Hills Creek, where water in the oil is known to be an issue? **Let's test several samples in several ways to be sure.** [See "ERDC ESTIMATE WITH TRACK CHANGES – Sulfide in Hydraulic Systems Outline_11042016.docx" and "Hydraulic Fluid Testing.msg"]

THIS IS A TOTAL OF 3 WATER SAMPLES + 18 OIL SAMPLES (1/2 liter, glass containers) + FILTERS TO ERDC ALTOGETHER, all on "ice".

From Blue River:

- Check the water for sulfur-reducing organisms and for sulfide and sulfate, pH, and zinc.
- Check 11 oil samples for water, zinc, sulfur, acid number, and sulfur-reducing organisms
    - Sample already taken that is pegging the meter
    - Samples from tops and bottoms of all 4 cylinders
    - Fresh sample from sump tank sample port
    - Sample from sump tank drain port – SPECIFICALLY ASK WHETHER WATER IS VISIBLE TO THE NAKED EYE IN THIS SAMPLE.
- Directly examine filter scrapings under microscope

From Cougar, which is very similar to Blue River, with the same oil, perhaps even from the same “batch” of oil, and is also known to have high acid number results. Cougar also has a heater on the sump tank.:

- Check the water for sulfur-reducing organisms and for sulfide and sulfate, pH, and zinc.
- Check 2 oil samples for water, zinc, sulfur, acid number, and sulfur-reducing organisms
    - From sump tank sample port
    - From sump tank drain port – SPECIFICALLY ASK WHETHER WATER IS VISIBLE TO THE NAKED EYE IN THIS SAMPLE.

From Hills Creek, which is NOT similar to Blue River:

- Check the water for sulfur-reducing organisms and for sulfide and sulfate, pH, and zinc.
- Check 2 oil samples for water, zinc, sulfur, acid number, and sulfur-reducing organisms
    - From sump tank sample port
    - From sump tank drain port – SPECIFICALLY ASK WHETHER WATER IS VISIBLE TO THE NAKED EYE IN THIS SAMPLE.

From NEW Chevron Rando HD 32 oil [See “Chevron Rando HD32.pdf”] in Project’s possession:

- Check for water, zinc, sulfur, acid number, and sulfur-reducing organisms

From NEW Chevron Clarity Hydraulic AW 32 oil [See “Chevron Clarity AW.pdf”] NOT in Project’s possession, but Project can get some:

- Check for water, zinc, sulfur, acid number, and sulfur-reducing organisms

From NEW Chevron Hydraulic Oil AW 32 [See “Chevron Hydraulic Oil AW.pdf”] in Project’s possession:

- Check for water, zinc, sulfur, acid number, and sulfur-reducing organisms

If we are agreed on the above, what do we do about it right now?

- Rich and April are working to determine/procure needed hardware to attach to existing ports to take samples.
- Dave will be able to get KTR in to take samples, and can provide sample bottles, and shipment “on ice” to ERDC.
- Glass bottles, ½ liter,
- Ask Victor for revised estimate, MIPR $, and “go”? We do get to continue on the BOI team through lab test results and finalizing path forward once we have that data. YAY! Discussed verbal estimate was that ERDC/lab work could be done in January.

Ultimate Path Forward, to be modified if test results lead to other conclusions:

Get rid of Blue River’s in-service hydraulic oil:

- Using KTR in SCBA gear, hazardous waste disposal, etc.?
- Using equipment such as High Purity NorthWest’s kidney-loop vacuum dehydrator WITH H2S REMOVAL system – apparently the dehydrator, instead of venting gas to the room, sends it through an additional filter that renders the H2S inert – “turns it to rust”. [See “Oil Purification.msg”] They can put one together that can go down the manlift. One of these could be used as an additional “normal” kidney-loop but could also go all over the District in case someone else runs into H2S in the future. Then personnel perhaps without SCBA, but with ventilation & monitoring just in case, could remove oil as normal?
- Either way, wipe down accessible wetted surfaces with lint-free cloths.

Replace hydraulic oil:

- With new oil, but the same type already in use.
- With NEW new oil – that has no ZDDP in it at all – such as Chevron Clarity Hydraulic AW 32 oil. This would be Incompatible with Rando HD oil, so system would need to be flushed at least twice with the new oil before the final fill. It may or may not be incompatible with Chevron Hydraulic Oil AW – Cathy will call Chevron to ask.

Keep it very dry AND MAYBE COOLER:

- Dedicate kidney loop?
- Increase frequency of breather replacement
- REPLACE HEATER OR REDUCE TEMPERATURE SETTING?

Appendix B: Product Data Sheet (PDS) and MSDS for Chevron-Rando Oil®

RANDO® HD
10, 22, 32, 46, 68, 100, 150, 220, 320

PRODUCT DESCRIPTION

Rando® HD oils are formulated with premium base oil technology and designed to give robust protection to hydraulic pumps in mobile and stationary systems.

CUSTOMER BENEFITS

Rando HD oils deliver value through:

- **Long equipment life** — Special antiwear additive package minimizes wear by protecting surfaces when load causes breakdown of the lubricant film.
- **Minimized downtime** — Effective rust and oxidation inhibitor system helps prevent the production of abrasive particles from rust formation, and deposits, varnishes and sludges from oil breakdown, which can damage equipment surfaces and seals, and block filters prematurely.
- **Smooth operation** — Good hydrolytic stability and water separation characteristics promote excellent filterability in the presence of water contamination. Good anti-foam and air release help ensure smooth operation and system efficiency.
- **Optimal oil service life** — High oxidation stability resists oil thickening and deposit formation in service, minimizing the possibility of an unscheduled change of hydraulic fluid.

FEATURES

Rando HD **ISO 32**, **46**, and **68** are formulated with Group II base stocks.

Rando HD **ISO 100**, **150**, **220**, and **320** are designed for lubricant applications requiring an AGMA R&O gear oil lubricant in the applicable viscosity grade.

Rando HD oils provide excellent:

- antiwear protection
- oxidation and corrosion inhibition
- foam and aeration suppression

Under moderate loads and temperatures, the high viscosity index of Rando HD oils help ensure good film strength between metal surfaces and is further enhanced by antiwear additive protection.

APPLICATIONS

Rando HD **ISO 10** and **22** can be used as spindle lubricants where zinc-free oils are not a requirement.

Rando HD **ISO 32**, **46**, or **68** are recommended for:

- vane-, piston-, or gear-type pumps, especially where pressures exceed 1000 psi
- lightly loaded reciprocating compressors

Rando HD **ISO 100**, **150**, **220**, or **320** are recommended for applications where AGMA rust and oxidation inhibited oils are required:

- hydraulic equipment reduction gears where EP is not required
- plain and antifriction bearings
- circulating oil systems

Rando HD oils are approved for:

- **Eaton-Vickers** 35VQ25A pump, M-2950-S (Mobile) and I-286-S (Stationary) (ISO 32, 46, 68)
- **Fives Cincinnati** (formerly MAG Cincinnati, Cin Machine, Cin Milacron) P-68 (ISO 32), P-70 (ISO 46), P-69 (ISO 68)
- **Parker Hannifin (Denison)** HFO, HF1, HF2, T6H2OC (ISO 32, 46, 68)

Rando HD oils meet the requirements of:

- **AFNOR** NF E 48-603 HM (ISO 32, 46, 68)
- **ANSI/AGMA** 9005-E02, *Industrial Gear Lubrication*, for gear lubrication as rust and oxidation inhibited gear oils (ISO 46, 68, 100, 150, 220)

Product(s) manufactured in the USA, Colombia and El Salvador.
Always confirm that the product selected is consistent with the original equipment manufacturer's recommendation for the equipment operating conditions and customer's maintenance practices.

A **Chevron** company product

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Rando® HD – Continued

- **ASTM** D6158 HM (ISO 32, 46, 68, 100, 150)
- **Bosch Rexroth** former specification RE 90220-01 (ISO 32, 46, 68)
- **DIN** 51524-2 (ISO 32, 46, 68)
- **General Motors** LS2 Specification, LH for anti-wear hydraulic fluids (ISO 32, 46, 68)
- **ISO** 11158 L-HM
- **Joy** HO-S (ISO 68)
- **US Steel** 126, 127 (ISO 32, 46, 68)

Rando HD **32, 46, 68, 100, 150, 220, 320** are registered by **NSF** and are acceptable as lubricants where there is no possibility of food contact (H2) in and around food processing areas. The NSF Nonfood Compounds Registration Program is a continuation of the USDA product approval and listing program, which is based on meeting regulatory requirements of appropriate use, ingredient review and labeling verification.

Do not use in high pressure systems in the vicinity of flames, sparks and hot surfaces. Use only in well ventilated areas. Keep container closed.

Do not use in breathing air apparatus or medical equipment.

TYPICAL TEST DATA

ISO Grade	10	22	32	46	68
Product Number	*273252*	*273276*	*273277*	*273278*	*273279*
SDS/MSDS Number *USA* *Colombia* *El Salvador*	 *23706* – –	 *23548* – –	 *23556* *33476* *33477*	 *23556* *33476* *33477*	 *23556* *33476* *33477*
AGMA Grade	–	–	–	1	2
API Gravity	27.7	33.7	32.6	31.8	31.6
Viscosity, Kinematic cSt at 40°C cSt at 100°C	 10.3 2.5	 23.1 4.4	 30.4 5.2	 43.7 6.5	 64.6 8.4
Viscosity, Saybolt SUS at 100°F SUS at 210°F	 63 35	 120 41	 157 44	 225 48	 334 54
Viscosity Index	48	98	99	97	98
Flash Point, °C(°F)	154(309)	177(351)	220(428)	226(439)	235(455)
Pour Point, °C(°F)	-39(-38)	-36(-33)	-33(-27)	-30(-22)	-30(-22)
Oxidation Stability Hours to 2.0 mg KOH/g acid number, ASTM D943	–	–	>5000	>5000	>5000

Minor variations in product typical test data are to be expected in normal manufacturing.

Always confirm that the product selected is consistent with the original equipment manufacturer's recommendation for the equipment operating conditions and customer's maintenance practices.

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TYPICAL TEST DATA

ISO Grade	100	150	220	320
Product Number	*273228*	*273280*	*273281*	277316
SDS/MSDS Number				
USA	*23550*	*23550*	*23550*	23550
Colombia	*33474*	*33474*	—	—
El Salvador	*33475*	*33475*	—	—
AGMA Grade	3	4	5	6
API Gravity	30.1	29.7	28.5	27.4
Viscosity, Kinematic				
cSt at 40°C	95.0	143	209	304
cSt at 100°C	11.0	14.2	18.2	23.4
Viscosity, Saybolt				
SUS at 100°F	495	751	1105	1617
SUS at 210°F	64	76	93	117
Viscosity Index	100	97	96	96
Flash Point, °C(°F)	250(482)	260(500)	271(520)	277(531)
Pour Point, °C(°F)	-15(+5)	-12(+10)	-12(+10)	-12(+10)
Oxidation Stability Hours to 2.0 mg KOH/g acid number, ASTM D943	>2000	>1500	>1000	>1000

Minor variations in product typical test data are to be expected in normal manufacturing.

Always confirm that the product selected is consistent with the original equipment manufacturer's recommendation for the equipment operating conditions and customer's maintenance practices.

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Safety Data Sheet

SECTION 1 PRODUCT AND COMPANY IDENTIFICATION

Rando HD 32, 46, 68

Product Use: Hydraulic Oil
Product Number(s): 273277, 273278, 273279
Company Identification
Chevron Products Company
a division of Chevron U.S.A. Inc.
6001 Bollinger Canyon Rd.
San Ramon, CA 94583
United States of America
www.chevronlubricants.com

Transportation Emergency Response
CHEMTREC: (800) 424-9300 or (703) 527-3887
Health Emergency
Chevron Emergency Information Center: Located in the USA. International collect calls accepted. (800) 231-0623 or (510) 231-0623
Product Information
email : lubemsds@chevron.com
Product Information: 1 (800) 582-3835, LUBETEK@chevron.com

SECTION 2 HAZARDS IDENTIFICATION

CLASSIFICATION: Not classified as hazardous according to 29 CFR 1910.1200 (2012).

HAZARDS NOT OTHERWISE CLASSIFIED: Not Applicable

SECTION 3 COMPOSITION/ INFORMATION ON INGREDIENTS

COMPONENTS	CAS NUMBER	AMOUNT
Highly refined mineral oil (C15 - C50)	Mixture	70 - 99 %weight

SECTION 4 FIRST AID MEASURES

Description of first aid measures
Eye: No specific first aid measures are required. As a precaution, remove contact lenses, if worn, and flush eyes with water.
Skin: No specific first aid measures are required. As a precaution, remove clothing and shoes if contaminated. To remove the material from skin, use soap and water. Discard contaminated clothing and shoes or thoroughly clean before reuse.
Ingestion: No specific first aid measures are required. Do not induce vomiting. As a precaution, get medical advice.
Inhalation: No specific first aid measures are required. If exposed to excessive levels of material in the air, move the exposed person to fresh air. Get medical attention if coughing or respiratory discomfort occurs.

Most important symptoms and effects, both acute and delayed
IMMEDIATE HEALTH EFFECTS
Eye: Not expected to cause prolonged or significant eye irritation.
Skin: Contact with the skin is not expected to cause prolonged or significant irritation. Contact with the skin is not expected to cause an allergic skin response. Not expected to be harmful to internal organs if absorbed through the skin. High-Pressure Equipment Information: Accidental high-velocity injection under the skin of materials of this type may result in serious injury. Seek medical attention at once should an accident like this occur. The initial wound at the injection site may not appear to be serious at first; but, if left untreated, could result in disfigurement or amputation of the affected part.

Ingestion: Not expected to be harmful if swallowed.
Inhalation: Not expected to be harmful if inhaled. Contains a petroleum-based mineral oil. May cause respiratory irritation or other pulmonary effects following prolonged or repeated inhalation of oil mist at airborne levels above the recommended mineral oil mist exposure limit. Symptoms of respiratory irritation may include coughing and difficulty breathing.

DELAYED OR OTHER HEALTH EFFECTS: Not classified

Indication of any immediate medical attention and special treatment needed
Note to Physicians: In an accident involving high-pressure equipment, this product may be injected under the skin. Such an accident may result in a small, sometimes bloodless, puncture wound. However, because of its driving force, material injected into a fingertip can be deposited into the palm of the hand. Within 24 hours, there is usually a great deal of swelling, discoloration, and intense throbbing pain. Immediate treatment at a surgical emergency center is recommended.

SECTION 5 FIRE FIGHTING MEASURES

EXTINGUISHING MEDIA: Use water fog, foam, dry chemical or carbon dioxide (CO_2) to extinguish flames.
Unusual Fire Hazards: Leaks/ruptures in high pressure system using materials of this type can create a fire hazard when in the vicinity of ignition sources (eg. open flame, pilot lights, sparks, or electric arcs).

PROTECTION OF FIRE FIGHTERS:
Fire Fighting Instructions: This material will burn although it is not easily ignited. See Section 7 for proper handling and storage. For fires involving this material, do not enter any enclosed or confined fire space without proper protective equipment, including self-contained breathing apparatus.
Combustion Products: Highly dependent on combustion conditions. A complex mixture of airborne solids, liquids, and gases including carbon monoxide, carbon dioxide, and unidentified organic compounds will be evolved when this material undergoes combustion.

SECTION 6 ACCIDENTAL RELEASE MEASURES

Protective Measures: Eliminate all sources of ignition in vicinity of spilled material.
Spill Management: Stop the source of the release if you can do it without risk. Contain release to prevent further contamination of soil, surface water or groundwater. Clean up spill as soon as possible, observing precautions in Exposure Controls/Personal Protection. Use appropriate techniques such as applying non-combustible absorbent materials or pumping. Where feasible and appropriate, remove contaminated soil. Place contaminated materials in disposable containers and dispose of in a manner consistent with applicable regulations.
Reporting: Report spills to local authorities and/or the U.S. Coast Guard's National Response Center at (800) 424-8802 as appropriate or required.

SECTION 7 HANDLING AND STORAGE

General Handling Information: Avoid contaminating soil or releasing this material into sewage and drainage systems and bodies of water.
Precautionary Measures: DO NOT USE IN HIGH PRESSURE SYSTEMS in the vicinity of flames, sparks and hot surfaces. Use only in well ventilated areas. Keep container closed.

Static Hazard: Electrostatic charge may accumulate and create a hazardous condition when handling this material. To minimize this hazard, bonding and grounding may be necessary but may not, by themselves, be sufficient. Review all operations which have the potential of generating and accumulating an electrostatic charge and/or a flammable atmosphere (including tank and container filling, splash filling, tank cleaning, sampling, gauging, switch loading, filtering, mixing, agitation, and vacuum truck operations) and use appropriate mitigating procedures.
Container Warnings: Container is not designed to contain pressure. Do not use pressure to empty container or it may rupture with explosive force. Empty containers retain product residue (solid, liquid, and/or vapor) and can be dangerous. Do not pressurize, cut, weld, braze, solder, drill, grind, or expose

such containers to heat, flame, sparks, static electricity, or other sources of ignition. They may explode and cause injury or death. Empty containers should be completely drained, properly closed, and promptly returned to a drum reconditioner or disposed of properly.

SECTION 8 EXPOSURE CONTROLS/PERSONAL PROTECTION

GENERAL CONSIDERATIONS:
Consider the potential hazards of this material (see Section 2), applicable exposure limits, job activities, and other substances in the work place when designing engineering controls and selecting personal protective equipment. If engineering controls or work practices are not adequate to prevent exposure to harmful levels of this material, the personal protective equipment listed below is recommended. The user should read and understand all instructions and limitations supplied with the equipment since protection is usually provided for a limited time or under certain circumstances.

ENGINEERING CONTROLS:
Use in a well-ventilated area.

PERSONAL PROTECTIVE EQUIPMENT
Eye/Face Protection: No special eye protection is normally required. Where splashing is possible, wear safety glasses with side shields as a good safety practice.
Skin Protection: No special protective clothing is normally required. Where splashing is possible, select protective clothing depending on operations conducted, physical requirements and other substances in the workplace. Suggested materials for protective gloves include: 4H (PE/EVAL), Nitrile Rubber, Silver Shield, Viton.
Respiratory Protection: No respiratory protection is normally required.
If user operations generate an oil mist, determine if airborne concentrations are below the occupational exposure limit for mineral oil mist. If not, wear an approved respirator that provides adequate protection from the measured concentrations of this material. For air-purifying respirators use a particulate cartridge. Use a positive pressure air-supplying respirator in circumstances where air-purifying respirators may not provide adequate protection.

Occupational Exposure Limits:

Component	Agency	TWA	STEL	Ceiling	Notation
Highly refined mineral oil (C15 - C50)	OSHA Z-1	5 mg/m3	--	--	--
Highly refined mineral oil (C15 - C50)	ACGIH	5 mg/m3	10 mg/m3	--	--

Consult local authorities for appropriate values.

SECTION 9 PHYSICAL AND CHEMICAL PROPERTIES

Skin Sensitization: The skin sensitization hazard is based on evaluation of data for product components.

Acute Dermal Toxicity: The acute dermal toxicity hazard is based on evaluation of data for product components.

Acute Oral Toxicity: The acute oral toxicity hazard is based on evaluation of data for product components.

Acute Inhalation Toxicity: The acute inhalation toxicity hazard is based on evaluation of data for product components.
Acute Toxicity Estimate: Not Determined

Germ Cell Mutagenicity: The hazard evaluation is based on data for components or a similar material.

Carcinogenicity: The hazard evaluation is based on data for components or a similar material.

Reproductive Toxicity: The hazard evaluation is based on data for components or a similar material.

Specific Target Organ Toxicity - Single Exposure: The hazard evaluation is based on data for components or a similar material.

Specific Target Organ Toxicity - Repeated Exposure: The hazard evaluation is based on data for components or a similar material.

ADDITIONAL TOXICOLOGY INFORMATION:
This product contains petroleum base oils which may be refined by various processes including severe solvent extraction, severe hydrocracking, or severe hydrotreating. None of the oils requires a cancer warning under the OSHA Hazard Communication Standard (29 CFR 1910.1200). These oils have not been listed in the National Toxicology Program (NTP) Annual Report nor have they been classified by the International Agency for Research on Cancer (IARC) as; carcinogenic to humans (Group 1), probably carcinogenic to humans (Group 2A), or possibly carcinogenic to humans (Group 2B).
These oils have not been classified by the American Conference of Governmental Industrial Hygienists (ACGIH) as: confirmed human carcinogen (A1), suspected human carcinogen (A2), or confirmed animal carcinogen with unknown relevance to humans (A3).

SECTION 12 ECOLOGICAL INFORMATION

ECOTOXICITY
This material is not expected to be harmful to aquatic organisms.
The product has not been tested. The statement has been derived from the properties of the individual components.

MOBILITY
No data available.

PERSISTENCE AND DEGRADABILITY
This material is not expected to be readily biodegradable. The biodegradability of this material is based on an evaluation of data for the components or a similar material.
The product has not been tested. The statement has been derived from the properties of the individual components.

POTENTIAL TO BIOACCUMULATE
Bioconcentration Factor: No data available.
Octanol/Water Partition Coefficient: No data available

SECTION 13 DISPOSAL CONSIDERATIONS

Use material for its intended purpose or recycle if possible. Oil collection services are available for used oil recycling or disposal. Place contaminated materials in containers and dispose of in a manner consistent with applicable regulations. Contact your sales representative or local environmental or health authorities for approved disposal or recycling methods.

SECTION 14 TRANSPORT INFORMATION

The description shown may not apply to all shipping situations. Consult 49CFR, or appropriate Dangerous Goods Regulations, for additional description requirements (e.g., technical name) and mode-specific or quantity-specific shipping requirements.

DOT Shipping Description: NOT REGULATED AS A HAZARDOUS MATERIAL UNDER 49 CFR

IMO/IMDG Shipping Description: NOT REGULATED AS DANGEROUS GOODS FOR TRANSPORT UNDER THE IMDG CODE

ICAO/IATA Shipping Description: NOT REGULATED AS DANGEROUS GOODS FOR TRANSPORT UNDER ICAO

Transport in bulk according to Annex II of MARPOL 73/78 and the IBC code:
Not applicable

SECTION 15 REGULATORY INFORMATION

EPCRA 311/312 CATEGORIES:	1. Immediate (Acute) Health Effects:	NO
	2. Delayed (Chronic) Health Effects:	NO
	3. Fire Hazard:	NO
	4. Sudden Release of Pressure Hazard:	NO
	5. Reactivity Hazard:	NO

REGULATORY LISTS SEARCHED:

01-1=IARC Group 1	03=EPCRA 313
01-2A=IARC Group 2A	04=CA Proposition 65
01-2B=IARC Group 2B	05=MA RTK
02=NTP Carcinogen	06=NJ RTK
	07=PA RTK

No components of this material were found on the regulatory lists above.

CHEMICAL INVENTORIES:
All components comply with the following chemical inventory requirements: AICS (Australia), DSL (Canada), ENCS (Japan), IECSC (China), KECI (Korea), PICCS (Philippines), TSCA (United States).

NEW JERSEY RTK CLASSIFICATION:
Under the New Jersey Right-to-Know Act L. 1983 Chapter 315 N.J.S.A. 34:5A-1 et. seq., the product is to be identified as follows: PETROLEUM OIL (Hydraulic oil)

SECTION 16 OTHER INFORMATION

NFPA RATINGS: Health: 0 Flammability: 1 Reactivity: 0

HMIS RATINGS: Health: 0 Flammability: 1 Reactivity: 0
(0-Least, 1-Slight, 2-Moderate, 3-High, 4-Extreme, PPE:- Personal Protection Equipment Index recommendation, *- Chronic Effect Indicator). These values are obtained using the guidelines or published evaluations prepared by the National Fire Protection Association (NFPA) or the National Paint and Coating Association (for HMIS ratings).

REVISION STATEMENT: This revision updates the following sections of this Safety Data Sheet: 1 - 16
Revision Date: FEBRUARY 05, 2016

ABBREVIATIONS THAT MAY HAVE BEEN USED IN THIS DOCUMENT:

TLV - Threshold Limit Value	TWA - Time Weighted Average
STEL - Short-term Exposure Limit	PEL - Permissible Exposure Limit
GHS - Globally Harmonized System	CAS - Chemical Abstract Service Number
ACGIH - American Conference of Governmental Industrial Hygienists	IMO/IMDG - International Maritime Dangerous Goods Code
API - American Petroleum Institute	SDS - Safety Data Sheet
HMIS - Hazardous Materials Information System	NFPA - National Fire Protection Association (USA)
DOT - Department of Transportation (USA)	NTP - National Toxicology Program (USA)
IARC - International Agency for Research on	OSHA - Occupational Safety and Health Administration

Cancer	
NCEL - New Chemical Exposure Limit	EPA - Environmental Protection Agency
SCBA - Self-Contained Breathing Apparatus	

Prepared according to the 29 CFR 1910.1200 (2012) by Chevron Energy Technology Company, 6001 Bollinger Canyon Road San Ramon, CA 94583.

The above information is based on the data of which we are aware and is believed to be correct as of the date hereof. Since this information may be applied under conditions beyond our control and with which we may be unfamiliar and since data made available subsequent to the date hereof may suggest modifications of the information, we do not assume any responsibility for the results of its use. This information is furnished upon condition that the person receiving it shall make his own determination of the suitability of the material for his particular purpose.

Appendix C: Quality Assurance Plan

Quality Assurance Project Plan

"Blue River Study - Investigation of Sulfide in Hydraulic Oil"

Prepared by the U.S. Army Corps of Engineers

January 28 to March 22, 2017

SECTION 1.0 BACKGROUND

1.1 Purpose of the Study

Recently, hydrogen sulfide emissions were found during the maintenance of a hydraulic system at the Blue River, Cougar, and Hills Creek Dam. Hydrogen sulfide is potentially toxic and explosive. So, determining the cause of this gas is needed. There are three possibilities – thermal transformation of ZDDP (a sulfur containing additive to the hydraulic oil), abiotic hydrolysis reaction of the ZDDP, or microbially mediated reduction of sulfur. ERDC will support the Portland District (NWP) with studies to explore sulfide in the oil and associated water. We will also look for evidence of sulfur reduction by microbial activity. These studies coupled with studies to be conducted by NWP should allow for us to narrow down the possible causes of this sulfide gas.

1.2 Project Objective

1) This project has two objectives. The first is to explore sulfide in the oil and associated water and look for evidence of sulfur reduction by microbial activity. The second goal is to narrow down the possible causes of this sulfide gas.

1.3 Project Organization

Dr. Victor Medina – Project Lead

Michelle Wynter – Quality Assurance Plan, filter study, data analysis

Dr. Cari Jung – Genetic studies for Sulfate Reducing Bacteria

Amber Russell – Coordination with contract laboratories, analysis of water samples

SECTION 2.0 SAMPLING / MONITORING PROCEDURES

We will study samples from 3 dams (Blue River, Cougar and Hills Creek) that have had reported hydrogen sulfide issues. The total number of samples are estimated at 18 hydraulic oil samples and 3 water samples. ERDC will also receive filter samples.

SECTION 3.0 TESTING AND MEASUREMENT PROTOCOLS

3.1 Measurements to be conducted by ERDC

ERDC will conduct the following measurements using the following methods:

- Survey Hydraulic oil samples and water samples for the presence and activity of dissimilatory sulfate reduction. A PCR-based survey targeting the conserved dissimilatory sulfate reduction (DSR) gene was employed. The presence of this gene would indicate at a genetic level the physiological potential of sponsor-selected samples toward the reduction of sulfate and the presence of sulfate reducing bacteria (SRBs) that may be responsible for biofouling.
- The hydraulic filters and scrapings from filters using binocular microscope. Interesting portions will also be investigated via scanning electron microscopy.

3.2 Other analyses were conducted by a certified commercial laboratory.

Conductivity, pH, total sulfur, sulfide, sulfate, and zinc analyses were conducted for the water samples. The oil samples were analyzed for water content, zinc, sulfur, acid number, and sulfur reducing microorganisms using a genetic probe.

SECTION 4.0 DATA REPORTING

4.1 Literature study

A Literature search will be completed on most likely ways that H2S was produced under in-service conditions at Blue River, Cougar, and Hills Creek Dam for lubricant used.

4.2 Report

ERDC will prepare a report on its methods and findings. The ERDC reporting effort could be integrated into a larger report, if that is desirable.

Appendix D: Report on Sulfur Reducing Microbial Probe Investigation

FINAL REPORT

Survey of sulfate reducing bacteria in hydraulic oils and water samples from USACE Portland.

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Purpose. Survey Hydraulic oil samples and water samples sent from the USACE Portland district for the presence and activity of dissimilatory sulfate reduction.

Materials and Methods. A PCR-based survey targeting the conserved dissimilatory sulfate reduction (DSR) gene was employed. The presence of this gene would indicate at a genetic level the physiological potential of sponsor-selected samples toward the reduction of sulfate and the presence of sulfate reducing bacteria (SRBs) that may be responsible for biofouling. A physiological diagnostic test known colloquially as a BART test was also performed on 18 select samples.

Aliquots were taken from the samples and poured into into a 50 ml Falcon tube. The samples were further split by placing 15 ml into a BART test vial for SRBs (http://www.hach.com/bart-test-sulfate-reducing-bacteria-pk-9/product-downloads?id=7640250866) and the remaining 30 ml were centrifuged to separate the debris/cells from each water/oil sample. Sample #25 had less volume than the other samples and we received only 30 ml once the other groups took their portions. Also the filter samples (#21-24) were obtained by dissecting the apparatus and taking the two innermost layers from each. A portion of the filter material was cut away and 0.25 g was added to the DNA extraction kit as detailed for the remaining samples below. The debris/cells from liquid samples were washed with sterile water and centrifuged again. The cleaned debris/cells were extracted with a MoBio Power Soil DNA extraction kit following the manufacturer's instructions. Samples were processed by standard DNA extraction techniques and traditional PCR was performed. Each sample was PCR amplified with 16S rDNA primers (Table 1) as a quality control check for amplification of the isolated DNA; this targets ribosomal DNA and is always present if bacteria are present; a negative reaction means the sample has extremely low or absent biomass. DNA samples were then amplified with the DSR primer sets specific for SRBs (Table 1).

Table 1. Primers and conditions for targeted PCR.

Primer	Primers (5'-3')	PCR parameters	Reference
*dsr*1	F - ACSCACTGGAAGCACG R - GTGGAGCCGTGCATGTT	95°C for 10 min, 40 cycles of 15 s at 94°C, 1 min at 59°C, 45 s at 72°C	Leloup 2007
16S rRNA	F - AGAGTTTGATCATGGCTCAG R -TACGGYTACCTTGTTACGACTT	95°C for 5 min; 32 cycles of 94°C for 45 s 55°C for 45 s and 72°C for 1 min; and a final extension of 72°C for 10 min	Krause 2000

Each of the 11 samples successfully amplified (Figure 2). DNA samples were then amplified with the primer sets specific for three gene targets (Table 1).

Results and Discussion. Samples were PCR amplified with primers for a ribosomal gene present in all bacteria as a control to determine the ability of the samples to be amplified by DNA and/or as an assessment of the presence or absence of bacteria. Only 10 samples appeared to be either capable of amplification or contain bacteria. Nevertheless, all samples were then PCR amplified for the dissimilatory sulfate reduction pathway, *dsr1*. There was no visual amplification of any of the samples with the DSR primers. In light of the 16S rDNA PCR results only those sample results that were positive for 16S can be trusted to be amplified and to have bacteria present. However, all of the samples were negative for the presence of the DSR gene and there may be either no or very limited numbers of SRBs in the source site.

As a further test for the presence of SRBs and bacteria in general, a physiological assessment of the samples was conducted on select samples. Samples were inoculated into a BART test which is used routinely in field testing for the presence of SRBs in water, soils, and industrial oils. All tested samples confirmed the results of PCR and were negative for SRB activity after 9 days. Furthermore, there was no evidence of anaerobic bacterial activity.

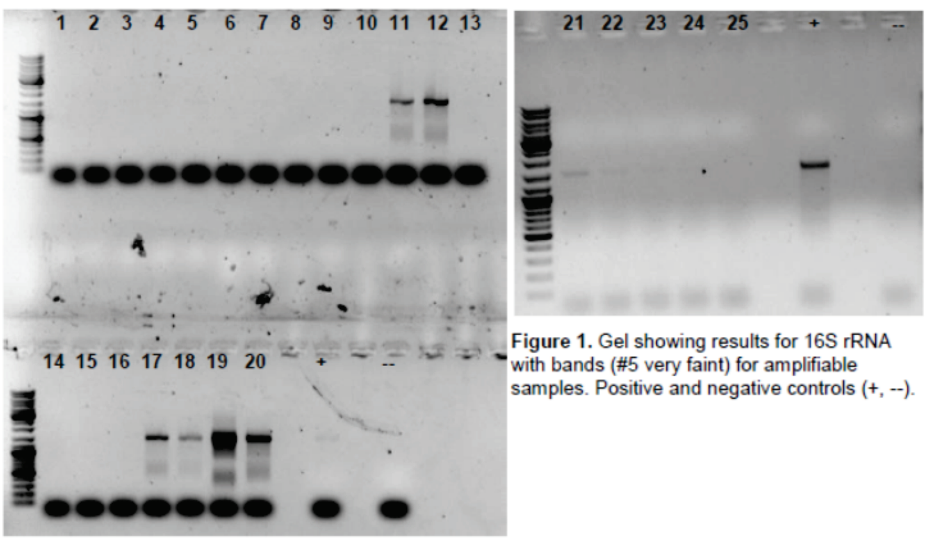

Figure 1. Gel showing results for 16S rRNA with bands (#5 very faint) for amplifiable samples. Positive and negative controls (+, --).

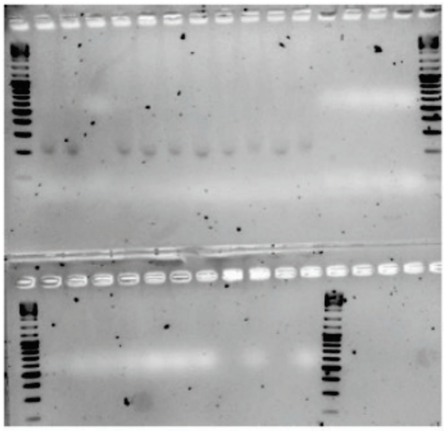

Figure 2. Gel showing negative results for DSR gene. Band should be located at the 3rd band from the bottom, above the faint bands that are seen in the first lanes.

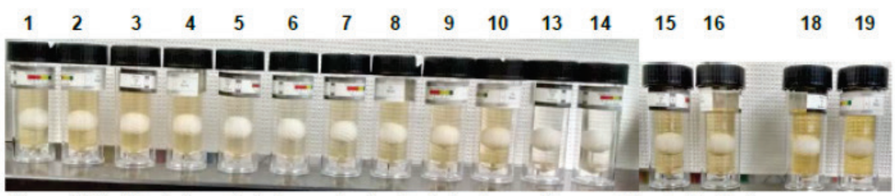

Figure 3. Bart tests for selected samples. Lack of cloudy growth around the ball indicates no or inconsequential numbers of anaerobic bacteria present. The lack of black precipitate indicates no sulfate reduction was occurring. The test spanned nine days and was observed daily.

Table 2. Summary of samples processed, biological tests run, and results.

sample #			Blue River Dam			16S PCR	DSR PCR	BART
1	BLR-20170126-001	10/18/2016	Grab	Hydraulic Oil	Original Oil Sample	–	–	–
2	BLR-20170126-002	1/26/2017	Grab	Hydraulic Oil	HPU oil sumo tank samole oort	–	–	–
3	BLR-20170126-003	1/26/2017	Grab	Hydraulic Oil	HPU oil sumo tank drain oort	–	–	–
25	BLR-20170126-004	1/26/2017	Grab	Hydraulic Oil	RO #1 Service Top		–	NA
4	BLR-20170126-005	1/26/2017	Grab	Hydraulic Oil	RO #1 Service Bottom	–	–	–
5	BLR-20170126-006	1/26/2017	Grab	Hydraulic Oil	RO #1 Emerency Top	+	–	–
6	BLR-20170126-007	1/26/2017	Grab	Hydraulic Oil	RO #1 Emergency Bottom	–	–	–
7	BLR-20170126-008	1/26/2017	Grab	Hydraulic Oil	RO #2 Service Too	–	–	–
8	BLR-20170126-009	1/26/2017	Grab	Hydraulic Oil	RO #2 Service Bottom	–	–	–
9	BLR-20170126-010	1/26/2017	Grab	Hydraulic Oil	RO #2 Emergency Too	–	–	–
10	BLR-20170126-011	1/26/2017	Grab	Hydraulic Oi	RO #2 Emergency Bottom	–	–	–
11	BLR-20170126-012	1/26/2017	Grab	Water	Drainage Sumo	+	–	NA
12	BLR-20170126-013	1/26/2017	Grab	Water	Reservoir near intake tower	+	–	NA
21	BLR-20170126-014	10/18/2016	inner layer (4)	Filter Cartridge	Original Oil Filter	+	–	NA
22	BLR-20170126-014	10/18/2016	innermost layer (5)	Filter Cartridge	Original Oil Filter	+	–	NA
23	BLR-20170126-015	10/18/2016	inner layer (4)	Filter Cartridge	Original Oil Filter	+	–	NA
24	BLR-20170126-015	10/18/2016	innermost layer (5)	Filter Cartridge	Original Oil Filter	–	–	NA
13	BLR-20170126-016	1/26/2017	Grab	Hydraulic Oil	Chevron Rando HD ISO 32 NEW oil	–	–	–
14	BLR-20170126-017	1/26/2017	Grab	Hydraulic Oil	Chevron Rando HD ISO 32 NEW oil	–	–	–
			Cougar Dam					
15	CGR-20170126-001	1/26/2017	Grab		HPU oil sumo tank samole oort	–	–	–
16	CGR-20170126-002	1/26/2017	Grab		HPU oil sumo tank drain oort	–	–	–
17	CGR-20170126-003	1/26/2017	Grab		Reservoir near intake tower	+	–	NA
			Hills Creek Dam					
18	HCR-20170126-001	1/26/2017	Grab		HPU oil sumo tank sample port	+	–	–
19	HCR-20170126-002	1/26/2017	Grab		HPU oil sumo tank drain oort	+	–	–
20	HCR-20170126-003	1/26/2017	Grab		Reservoir near intake tower	+	–	NA

References.

Krause, D.O., W.J. Smith, F.M. Ryan, R.I. Mackie, C.S. McSweeney. 1999. Use of 16S-rRNA based techniques to investigate the ecological succession of microbial populations in the immature lamb rumen: tracking of a specific strain of inoculated *Ruminococcus* and interactions with other microbial populations *in vivo*. Micob. Ecol. 38(4):365-376.

Leloup,J., A. Loy, N.J. Knab, C. Borowski, M. Wagner and B.B. Jørgensen. 2007. Diversity and abundance of sulfate-reducing microorganisms in the sulfate and methane zones of a marine sediment, Black Sea. Environ. Microbiol. 9(1):131–142.

Appendix E: Product Data Sheet (PDS) for Chevron AW Oil - Alternative to Rando Oil

CHEVRON HYDRAULIC OIL AW

32, 46, 68 & ISOCLEAN® Certified

PRODUCT DESCRIPTION

Chevron Hydraulic Oils AW are designed to give excellent hydraulic pump protection. Chevron Hydraulic Oils AW are available as ISOCLEAN® Certified Lubricants, which have been certified to meet specified ISO Cleanliness standards at point of delivery using industry leading filtration and testing technology. ISOCLEAN Certified products are the first step for contamination control and maximizing component life.

CUSTOMER BENEFITS

Chevron Hydraulic Oils AW deliver value through:

- **Good oxidation stability** — Provide good service life in high pressure service.
- **Rust and corrosion protection** — Give excellent protection against corrosion of both copper and steel, and passes the ASTM D665A distilled water rust test and ASTM D665B synthetic sea water rust test.
- **Minimum viscosity change** over a wide temperature range.
- **Good foam inhibition** — Contain special foam suppressant, minimizing both foaming and aeration problems.
- **Excellent antiwear properties**
- **Meets major pump manufacturer's requirements** — ISO 32, 46 and 68 meet the requirements of leading hydraulic pump manufacturers for antiwear-type hydraulic fluids in both vane- and piston-type pumps.
- **Good stability in the presence of water** by ASTM D2619 Hydrolytic Stability test and the Denison hybrid T6H20C Wet Pump test.
- **Good thermal stability** in the presence of copper and steel by the MAG Cincinnati Machine Thermal Stability, Procedure A, test.
- **Fast water separation** — Minimize rust problems by fast release of water.

CUSTOMER BENEFITS ISOCLEAN CERTIFIED

Chevron Hydraulic Oil AW ISOCLEAN Certified Lubricants deliver value through:

- **Ready to use** — Enables users to meet stringent original equipment manufacturers' cleanliness standards for fill lubricants.
- **Flexibility** — ISO Cleanliness targets can be customized to fit your business application needs.
- **Peace of mind** — Each delivery of Chevron ISOCLEAN Certified Lubricant includes an ISOCLEAN Certificate of Analysis.
- **OE fluid cleanliness requirements** — Customized to meet specific equipment manufacturers' fluid cleanliness requirements.

FEATURES

Chevron Hydraulic Oils AW are formulated with refined paraffinic base oils. They provide excellent antiwear protection, oxidation and corrosion inhibition, as well as foam and aeration suppression. All grades have excellent demulsibility characteristics.

Hydraulic systems, due to the nature of their operation, experience accelerated wear unless they are protected by clean, high quality antiwear hydraulic oils. Surging pressures in pumps and valves can increase metal-to-metal contact unless antiwear protection is present. The antiwear additives in Chevron Hydraulic Oils AW create a protective film on the metal surfaces. This protective film minimizes metal-to-metal contact, which is most severe in vane- and gear-type pumps. As hydraulic pressures increase over 1000 psi, the need for antiwear protection increases proportionally.

Product(s) manufactured in the USA.
Always confirm that the product selected is consistent with the original equipment manufacturer's recommendation for the equipment operating conditions and customer's maintenance practices.

A **Chevron** company product

1 July 2016
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Chevron Hydraulic Oil AW — Continued

Applications

Chevron Hydraulic Oils AW are versatile lubricants available in ISO viscosity grades 32, 46 and 68.

ISO 32, **46** and **68** grades are most commonly used for hydraulics with vane-, piston-, or gear-type pumps, especially where pressures exceed 1000 psi. They can also be used to lubricate lightly loaded reciprocating compressors.

Chevron Hydraulic Oils AW **32**, **46** and **68**:

- meet major pump manufacturer requirements including **Eaton-Vickers** 35VQ25A for M-2950-S (Mobile) and I-286-S (Stationary), **Parker Hannifin (Denison)** HF0/HF2/T6H20C, and **Bosch Rexroth Racine** Model S
- meet **ASTM** D6158 HM
- meet **DIN** 51524-2
- meet **ISO** 11158 L-HM
- meet **MAG Cincinnati, Cincinnati Machine** specifications P-68 (ISO 32), P-70 (ISO 46), and P-69 (ISO 68)

Chevron Hydraulic Oils AW 32, 46, 68 and ISOCLEAN® Certified 32, 46, 68 are registered by **NSF** and are acceptable as lubricants where there is no possibility of food contact (H2) in and around food processing areas. The NSF Nonfood Compounds Registration Program is a continuation of the USDA product approval and listing program, which is based on meeting regulatory requirements of appropriate use, ingredient review and labeling verification.

Please consult with your equipment manufacturer if equipment is operating outside normal operating conditions. Do not use in high pressure systems in the vicinity of flames, sparks and hot surfaces. Use only in well ventilated areas. Keep container closed.

Consult with your Chevron Lubricant Representative or Chevron ISOCLEAN Certified Lubricants Marketer to set specific ISO Cleanliness targets for your business application.

Typical Test Data

ISO Grade	32	46	68
Product Number	*255675*	*255674*	*255673*
Product Number *ISOCLEAN Certified*	*293130*	*293131*	*293132*
SDS Number	*7457*	*7457*	*7457*
API Gravity	32.6	31.8	31.6
Viscosity, Kinematic cSt at 40°C cSt at 100°C	 30.4 5.2	 43.7 6.5	 64.6 8.4
Viscosity, Saybolt SUS at 100°F SUS at 210°F	 157 44	 225 48	 334 55
Viscosity Index	98	98	99
Flash Point, °C(°F)	220(428)	226(439)	235(455)
Pour Point, °C(°F)	-25(-13)	-23(-9)	-22(-8)
Oxidation Stability Hours to 2.0 mg KOH/g acid number, ASTM D943	> 2000	> 2000	> 2000

Minor variations in product typical test data are to be expected in normal manufacturing.

Always confirm that the product selected is consistent with the original equipment manufacturer's recommendation for the equipment operating conditions and customer's maintenance practices.

1 July 2016
IO-110

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14. ABSTRACT

Hydrogen sulfide releases occurred during a routine maintenance process in a hydraulic oil system at Blue River Dam, Oregon. The project worked under the hypothesis that the sulfide emissions most likely resulted from reductive biological processes. Hydraulic oil samples were collected from the Blue River Dam, and from two other nearby dams with similar hydraulic systems, Hills Creek Dam, and Cougar Dam. Water samples from the reservoir were also collected. Sulfur was found in all the oil and water samples, however, no patterns with sulfur to other parameters (such as percent water or acid neutralization number) were found in the oil samples. A microscopic review of hydraulic filters did not show any evidence of bio-film accumulation. The use of sulfate reductive bacterial genetic probes did not find any microbial activity expected to form sulfide. These results rejected the hypothesis that the sulfide production was from microbial activity. The Authors now hypothesize that the sulfide reaction was from abiotic reactions of an additive, Zinc Dialkyldithiophosphate (ZDDP).

15. SUBJECT TERMS

Blue River Dam (Or.)
Hydraulic structures
Water quality
Hydrogen sulfide

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