

# Investigation of Lead Levels at the Cavity Processing Laboratory (CPL) in Industrial Building 4

January 5, 2018

Written by: Eric Korzeniowski Date: 1/5/18  
Eric Korzeniowski, Environmental Specialist

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Tim Ring, Engineering Associate

A Crawford Date: 1-6-2018  
Anthony Crawford, Accelerator Physicist

Reviewed by: Amber Kenney Date: 1/12/2018  
Amber Kenney, Deputy Chief Safety Officer

Bridget Iverson Date: 1/5/18  
Bridget Iverson, Environmental Protection Manager

Approved by: Martha E. Michels Date: 1-16-18  
Martha Michels, Chief Safety Officer



# Investigation of Lead Levels at the Cavity Processing Laboratory (CPL) in Industrial Building 4

September 1, 2017

Eric T. Korzeniowski, Tim Ring, Anthony Crawford

## Introduction

The Environmental Safety Health and Quality (ESH&Q) Section and Technical Division (TD) recently investigated the potential causes for unexpected high levels of lead (Pb) in the CPL wastewater. Environmental and technical experts of the ESH&Q Section and TD reviewed the current process and took a systematic approach to sampling the system. The following documents the history of managing CPL for permit compliance and the determination for a path forward.

## Background

The wastewater neutralization system at CPL processes the dilute acid wastes from the niobium<sup>(1)</sup> polishing process and blowdown wastewater from the process related air scrubber prior to discharge to the City of Batavia Municipal Public Owned Treatment Works.

Dilute acid wastewater and scrubber blowdown may include niobium compounds, as well as salts from hydrofluoric and sulfuric acids when combined with sodium hydroxide. Wastewater is generated in 125-gallon batches at a frequency of not more than thrice a week. Polishing wastewater is accumulated in a 300-gallon neutralization tank. Fume scrubber blowdown is stored in a separate 300-gallon tank located above the neutralization tank. Fume scrubber blowdown is fed by gravity into the neutralization tank until a pH level in the range of 6 to 8 is achieved. Neutralized wastewater will be discharged to the sewer approximately three times per week. Each neutralized batch of wastewater is sampled prior to discharge to the Fermilab sanitary sewer system. The Fermilab sanitary sewer discharges to the City of Batavia Municipal Sanitary sewer system.

As a result of these operations Fermilab was issued a Pretreatment and Discharge of Metal Finishing Rinsewaters permit from the Illinois Environmental Protection Agency (IEPA) with four special conditions (See Regulatory Review below). Samples are collected semi-annually and are submitted to First Environmental Laboratory (FEL) which tests for lead (as well as other pollutants) using the ICP Method 200.7.

Initial results in 2012 showed lead levels above the detection limit of 0.002 mg/L (0.064 mg/L). Because this was unexpected, an additional sample of the tap water was taken at CPL with a lead result of 0.004

mg/L. In March 2013, lead results were 0.0679 mg/L, just below the pretreatment permit 1-Day Max of 0.69 mg/L and above Fermilab's internal discharge limit of 0.25 mg/L (FESHM 8025, City Code of Batavia). Upon review with other lab operations it was determined that discharging would not cause the lab to violate the City Code of Batavia discharge limit at the site boundary and CPL wastewater was released to the sanitary system. No lead was detected until June 2016 (0.135 mg/L) again in December 2016 (0.164 mg/L) and in June 2017 (0.354 mg/L). Following the June 2017 result a decision was made by the Environmental Protection Group and TD to collect more data to better understand why lead was appearing in the system, the following EP note is the result of that investigation.

## Permit Review

The following special conditions for the CPL Pretreatment Permit were reviewed for applicability as a part of this investigation. The list includes specific regulations, descriptions, and notes or interpretations made during their review.

### Special Condition 1:

- The operation of the pretreatment facilities must be under the direct and active field supervision of a certified industrial treatment plant operator in accordance with the State of Illinois Rules and Regulations, Title 35, Subtitle C, Chapter 1, Part 312.

### Special Condition 2:

- The issuance of this permit does not relieve the permittee of the responsibility of complying with any limitations and provisions imposed by the City of Batavia.

### Special Condition 3:

- The issuance of this permit does not relieve the permittee of the responsibility of complying with 35 Ill. Adm. Code, Part 307 and/or the General Pretreatment Regulations (40 CFR 403) and any guidelines developed pursuant to Section 301, 306, or 307 of the Federal Clean Water Act of 1977. The guidelines developed for the Metal Finishing Point Source Category (40 CFR 433 Subpart A- Metal Finishing Subcategory) limit the pollutants from facilities as follows:

Pollutant	1-Day Max. (mg/L)	Monthly Avg. (mg/L)
Cyanide (total)	1.2	0.065
Copper	3.38	2.07
Nickel	3.98	2.38
Chromium (total)	2.77	1.71
Zinc	2.61	1.48
Lead	0.69	0.43
Cadmium	0.11	0.07

Silver	0.43	0.24
TTO	2.13	-----

(A) The compliance date for the metals was February 15, 1986.

(B) These numbers do not reflect a reduction in the numerical limitation due to the contributing flow of sanitary wastes, non-contact cooling water, and other dilutional wastewater not regulated by the limitations.

(C) Cyanide monitoring must take place after cyanide treatment and before dilution with other waste streams unless an adjustment is made to account for the dilution ratio of the cyanide waste stream flow to the effluent flow.

(D) TTO is the total toxic organics in the regulation. Compliance with TTO limitations was required on July 15, 1986

#### Special Condition 4

- Monitoring Requirements

(A) The permittee shall monitor semi-annually the pollutants listed in Special Condition 3.

(B) Sampling shall be done after the wastewater treatment system prior to entry into the sewer system.

(C) Sampling shall be conducted during a normal working day during normal working hours.

(D) Test results shall be submitted to annually to:

Illinois Environmental Protection Agency Bureau of Water Compliance Assurance  
Section 1021 North Grand Avenue East P. O. Box 19216-- '--Springfield, Illinois 62794-9276

U.S. Environmental Protection Agency- Region 5 Water Enforcement and Compliance Assurance Branch Attention: Newton Ellens WUC-15J 77 West Jackson Boulevard Chicago, Illinois 60604

## Process Review

The process review began with TD collecting lead results from various locations using a systematic approach to eliminate possible parts/elements that could have been contributing to higher than expected lead levels. Samples were collected and sent to First Environmental from the following locations:

1. Scrubber NaOH solution from the scrubber tank
2. NaOH from old drums using ultra-pure water to dilute

3. NaOH from new source using ultra-pure water to dilute
4. Electrolyte (sulfuric and hydrofluoric acid mix) diluted with ultra-pure water and neutralized with NaOH from new source
5. IB4 Tap water
6. Ultra-pure water from electropolishing storage tanks stored in the mezzanine

Additionally, TD purchased a photometer and collected samples at the following locations:

1. IB4 Chemistry lab ultrapure water supply: < 3 micrograms/L Pb
2. IB4 domestic water supply: 85 micrograms/L Pb

Notes:

a. The photometer's resolution is 1 microgram/L, but its accuracy is 3 micrograms/L. So, a reading of 0 micrograms/L could be from a sample with as much as 3 micrograms/L.

b. The measurement of IB4 domestic water (tap water) was non-trivial. There was calcium and magnesium in the untreated water which caused an interference with the photometric measurement of lead, resulting in an unrealistically low reading. To get the value stated in (2.) above, the IB4 domestic water was diluted by a factor of five with ultrapure (>19.9 MOhm-cm) ion free water. The photometer reading was then multiplied by a factor of five.

c. CPL typically use less than 10 gallons of domestic water for each ~ 150-gallon batch of rinsewater. The rest of the water is from the ultrapure water supply. This means that the lead content in the domestic water does not add much to the concentration in the discharged water. This leading to the determination that the domestic water did not appear to be the source of the problem, despite the presence of lead.

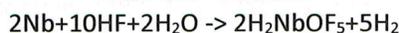
Following these results Anthony Crawford proposed the following:

Based on previous testing of the rinsewater from the cavity electropolish procedures, no detectable amount of lead was found (<3micrograms/L). Repeated tests of the rinsewater by FEL indicated lead concentrations that were roughly proportional to the amount of niobium that was removed during several electropolish procedures. This led to the theory of a potential interference during analysis leading to inaccurate results.

Further research determined that FEL uses mass spectrographic techniques to identify metals, specifically Inductively Coupled Plasma (ICP) testing. The principal waste product of niobium electropolishing with the hydrogen fluoride based electrolyte is:



from the reaction:



The atomic mass of  $\text{H}_2\text{NbOF}_5$  is 206 amu. The atomic mass of lead is 207 amu.

The close atomic mass indicated that the lead in the rinsewater was most likely due to an interference of the mass spectrographic signal from  $H_2NbOF_5$  and that there was, in reality, no significant amount of lead present.

Two identical rinsewater samples were then collected and analyzed by FEL using the original method, as well as an alternative method for that did not have the potential for interference from  $H_2NbOF_5$  (ICP-MS Method 200.8).

The report showed different results for the two identical samples. The FEL Project Manager stated the following in the report:

“The report is attached for lead analysis of the sample using both ICP Method 200.7 and ICP-MS Method 200.8.

We feel that the result from the ICP-MS is the result that appears to be unaffected by interferences that were observed in the ICP analysis. We did need to run the sample at a 10x on the ICP-MS due to the presence of an interference. The internal standard recovery at the 10x dilution was acceptable. The result reported for ICP-MS run reflect the 10x dilution.

The scan from the ICP run showed evidence of interferences. The instrument is set up to accommodate interferences, and the results are reproducible at different dilutions, but I feel the result is still suspect.”

See the attached report for results.

## Determination

Based on the FEL results the determination has been made that the oxyfluoroniobic acid was most likely being incorrectly detected as lead. Although the resulting impacts to oxyfluoroniobic acid when exposed to a sodium hydroxide solution remain uncertain, the FEL results and the process knowledge of the subject matter experts have all led to this determination.

Going forward EPG and TD will submit samples and request that the 200.8R5.4 method be used by FEL. This will also be addressed in the lab’s next permit renewal.



**First  
Environmental  
Laboratories, Inc.**

IL ELAP / NELAC Accreditation # 100292

1600 Shore Road • Naperville, Illinois 60563 • Phone (630) 778-1200 • Fax (630) 778-1233

August 01, 2017

Mr. Eric Korzeniowski  
**FERMI NATIONAL ACCELERATOR LABORATORY**  
P.O. Box 500  
MS 355  
Batavia, IL 60510-0500

Project ID: CPL #610021  
First Environmental File ID: 17-3817  
Date Received: July 19, 2017

Dear Mr. Eric Korzeniowski:

The above referenced project was analyzed as directed on the enclosed chain of custody record.

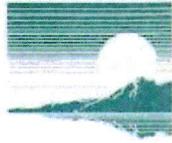
All Quality Control criteria as outlined in the methods and current IL ELAP/NELAP have been met unless otherwise noted. QA/QC documentation and raw data will remain on file for future reference. Our accreditation number is 100292 and our current certificate is number 004108: effective 03/24/2017 through 02/28/2018.

I thank you for the opportunity to be of service to you and look forward to working with you again in the future. Should you have any questions regarding any of the enclosed analytical data or need additional information, please contact me at (630) 778-1200.

Sincerely,

Lorrie Walker  
Project Manager

Page 1 of 5



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### Case Narrative

**FERMI NATIONAL ACCELERATOR LABORATORY**

Lab File ID: **17-3817**

Project ID: **CPL #610021**

Date Received: **July 19, 2017**

All quality control criteria, as outlined in the methods, have been met except as noted below or on the following analytical report.

The results in this report apply to the samples in the following table:

Laboratory Sample ID	Client Sample Identifier	Date/Time Collected
17-3817-001	170719TR01	7/19/2017 13:45
17-3817-002	170719TR02	7/19/2017 13:46

**Sample Batch Comments:**

Sample acceptance criteria were met.

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### Case Narrative

**FERMI NATIONAL ACCELERATOR LABORATORY**

Lab File ID: **17-3817**

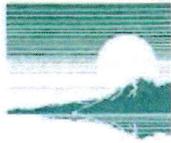
Project ID: **CPL #610021**

Date Received: **July 19, 2017**

All quality control criteria, as outlined in the methods, have been met except as noted below or on the following analytical report.

The following is a definition of flags that may be used in this report:

Flag	Description	Flag	Description
A	Method holding time is 15 minutes from collection. Lab analysis was performed as soon as possible.		
B	Analyte was found in the method blank.	L	LCS recovery outside control limits.
<	Analyte not detected at or above the reporting limit.	M	MS recovery outside control limits; LCS acceptable.
C	Sample received in an improper container for this test.	P	Chemical preservation pH adjusted in lab.
D	Surrogates diluted out; recovery not available.	Q	Result was determined by a GC/MS database search.
E	Estimated result; concentration exceeds calibration range.	S	Analysis was subcontracted to another laboratory.
G	Surrogate recovery outside control limits.	T	Result is less than three times the MDL value.
H	Analysis or extraction holding time exceeded.	W	Reporting limit elevated due to sample matrix.
J	Estimated result; concentration is less than routine RL but greater than MDL.	N	Analyte is not part of our NELAC accreditation or accreditation may not be available for this parameter.
RL	Routine Reporting Limit (Lowest amount that can be detected when routine weights/volumes are used without dilution.)	ND	Analyte was not detected using a library search routine; No calibration standard was analyzed.



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### Analytical Report

<b>Client:</b>	FERMI NATIONAL ACCELERATOR LABORATORY	<b>Date Collected:</b>	07/19/17
<b>Project ID:</b>	CPL #610021	<b>Time Collected:</b>	13:45
<b>Sample ID:</b>	170719TR01	<b>Date Received:</b>	07/19/17
<b>Sample No:</b>	17-3817-001	<b>Date Reported:</b>	08/01/17

Analyte	Result	R.L.	Units	Flags
<b>Total Metals</b>	<b>Method: 200.7R4.4</b>	<b>Preparation Method 200.7W</b>		
Analysis Date: 07/24/17		Preparation Date: 07/24/17		
Lead	0.3113	0.0050	mg/L	



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### Analytical Report

<b>Client:</b>	FERMI NATIONAL ACCELERATOR LABORATORY	<b>Date Collected:</b>	07/19/17
<b>Project ID:</b>	CPL #610021	<b>Time Collected:</b>	13:46
<b>Sample ID:</b>	170719TR02	<b>Date Received:</b>	07/19/17
<b>Sample No:</b>	17-3817-002	<b>Date Reported:</b>	08/01/17

Analyte	Result	R.L.	Units	Flags
<b>Total Metals</b>	<b>Method: 200.8R5.4</b>			
Analysis Date: 07/20/17				
Lead	< 0.020	0.002	mg/L	W S

