Publication No. 79-e09
WA-CR-1028

STATE OF WASHINGTON
Dixy Lee Ray
Governor

DEPARTMENT OF ECOLOGY
7272 Cleanwater Lane, Olympia, Washington 98504 206/753-2353

M E M O R A N D U M
June 20, 1979

To: Al Newman

From: Greg Cloud

Subject: Sandvik Special Metals Class II Inspection

Introduction

On January 23, 1978 Al Newman and I visited the Sandvik Special Metals facility at Finley. The industry representatives present were Charles Rutkowski and Claude Stacey. This industry is a major supplier of quality controlled dimensional zirconium tubing used as fuel containers in nuclear reactor cores. Only process water from the plant is discharged to the Columbia River. All sanitary wastewaters are discharged to the city of Kennewick sewage system. The process water contains machine workdown and etching (cleaning) solutions. These etching solutions contain nitric and hydrofluoric acids and are used to clean the zirconium tubing. The process water is piped into a dolomite lime pit intended to neutralize the acids and remove the fluorides. As the water trickles through the pit, CO_2 is liberated as a gas and calcium fluoride and magnesium flouride are formed. These insoluable compounds are retained at the surface of the dolomite. The water is then piped to a wet well prior to discharge to the Columbia River, segment No. 26-02-00.

Findings and Conclusions

The lime pit, with fresh dolomite lime, works well for buffering the acid process water. The flourides, from hydrofluoric acid, will be released from the pit at different rates as the exposed dolomite, $CaMg(CO_3)_2$, is converted to a rime of CaF_2 and MgF_2. As this rime is formed on the crushed dolomite, the pH buffering capacity is reduced and more fluorides are passed through the system. The oil and grease in the process water may also have a detrimental effect on the dolomite by forming a film to reduce surface area for the reaction to take place.

Solids may settle to some extent in the lime pit. Addition solids removal in the wet well is probably minimal. The rate of exchange in the wet well is fairly rapid so any settling that takes place would be from the heavier particulate matter. This industrial personnel did not mention that the wet well had ever been cleaned. As particulate matter accumulates in the wet well, the solids are pumped out with the rest of the effluent. Thus, the well probably provides little or no net removal of solids.

The whole waste abatement system could be improved over the present design. The dolomite in the lime pit is not failsafe and is probably not changed often enough. The industry uses the amount of fluoride escaping from the pit as an indicator for replenishment. The industry was out of compliance with fluoride at the time of inspection with a concentration of 16.7 mg/l. The permit allows 15 mg/l.

The NPDES permit limitations for flow seem to be exceeded most of the time. Sandvik's DMR's (self-monitoring reports) indicate maximum flows above permit limitations. The flow measuring device is an in-line meter in the discharge line downstream from the wet well pump. It could not be checked for accuracy. During the inspection the flow was exceeding limitations by nearly 40,000 gpd.

Recommendations

1. Better replenishment control on the dolomite lime.

2. The total oils and grease limitation on the NPDES permit should be changed from a 24-hour composite to a grab sample.

3. The flow should either be increased on the NPDES permit or the plant required to be in compliance with it.

A follow-up inspection will be made by Al Newman in mid-September 1979.

Review of Laboratory Procedures and Techniques

The only laboratory technique discussed with the Sandvik personnel (Claude Stacey) was the total suspended solids test. They appeared to be doing the solids test very well. This was verified by the laboratory comparison results. The laboratory comparisons for soluble fluoride were also very good. The zirconium determinations were also excellent and remarkably close, considering two different methods for determination were used. Sandvik used a colormetric method while the Department of Ecology contracted with Washington State University to do a neutron activation analysis utilizing a small nuclear reactor. The only test that leaves some doubt is that of total oils. When comparison samples were to be taken for total oils, one of the Sandvik lab personnel at first intended to use a plastic jug for the sample. When informed that plastic was unacceptable for oils determinations, he then procured a used, narrow-mouth, brown glass reagent jug from the trash barrel and then rinsed it out for the sample collection. This is not according to Standard Methods 14th Edition, which recommends that a

wide-mouth glass bottle be used. The method of collection should be a grab sample and not a 24-hour composite as stated in the NPDES permit. A surface grab sample is not recommended as it would bias the sample to the high side. The sample should be taken at the final discharge to the river, but as that is not feasible, the sample line from the wet well will have to suffice.

GC:cp

Attachments

Class II Field Review and Sample Collection
24 Hour Composite Sampler Installations

Sampler	Date and Time Installed	Location
1. Final Effluent aliquot - 250 ml/30 min.	1/23/78 1030 hrs.	Final Effluent (wet well sump)
2. aliquot -		
3. aliquot -		

Grab Samples

	Date and Time	Analysis	Sample Location
1.	1/24/78 1045 hrs	Temp, cond., pH	Final Effluent
2.	1/24/78 1045 hrs	Total oils (two samples)	(Wet well sump)
3.			
4.			
5.			
6.			

Flow Measuring Device

1. Type - in-line flow meter
2. Dimensions -

a. Meets standard criteria /__/ Yes

/__/ No Explain: In-line flow meter with no way to check for accuracy.

b. Accuracy check

	Actual Instan. Flow	Recorder Reading	Recorder Accuracy (% of inst. flow)
1.			
2.			
3.			

/__/ is within accepted 15% error limitations

/__/ is in need of calibration

Field Data

Parameter	Date and Time	Sample Location	Result
Temp.	1/24/78 1045 hrs.	Final Effluent	20.8 °C
Conductivity	1/24/78 1045 hrs.	Final Effluent	1100 µmhos/cm
pH	1/24/78 1045 hrs.	Final Effluent	3.3

DOE LABORATORY ANALYSIS

	DOE 24-hour Composite	Sandvik 24-Hour Composite
BOD_5 mg/l lbs/day	6 mg/l 15 lbs/day	4 mg/l 11.30 lbs/day
Sp. Conductivity µmhos/cm	1,670	2,380
$O\text{-}PO_4\text{-}P$ mg/l lbs/day	0.30 mg/l 0.78 lbs/day	0.40 mg/l 1.13 lbs/day
Total Solids	1130 mg/l 2922 lbs/day	1390 mg/l 3929 lbs/day
TNVS	921 mg/l 2381 lbs/day	1150 mg/l 3250 lbs/day
TSNVS	20 mg/l 52 lbs/day	20 mg/l 56.52 lbs/day
Iron mg/l lbs/day	0.3 mg/l 0.78 lbs/day	
Copper mg/l lbs/day	0.02 mg/l 0.52 lbs/day	
Chromium mg/l lbs/day	0.02 mg/l* 0.52 lbs/day*	
Manganese mg/l lbs/day	<0.02 mg/l <0.05 lbs/day	
Nickel mg/l lbs/day	<0.05 mg/l <0.31 lbs/day	
Cadmium mg/l lbs/day	<0.01 mg/l <0.03 lbs/day	
Zinc mg/l lbs/day	0.036 mg/l 0.09 lbs/day	
Lead mg/l lbs/day	<0.05 mg/l <0.13 lbs/day	

*Approximate

	DOE Analysis		Sandvik Special Metals Analysis		
	DOE 24-hour Composite	Sandvik 24-hour Composite	DOE 24-hour Composite	Sandvik 24-hour Composite	NPDES Daily Maximum
TSS mg/l lbs/day	24 mg/l 62 lbs/day	26 mg/l 73.5 lbs/day	21.2 mg/l 53 lbs/day	25.1 mg/l 71.1 lbs/day	30 mg/l 75 lbs/day
Total Plant Flow MGD	0.31 mgd*	0.3389 mgd	0.30 mgd#	0.3389 mgd	0.3 mgd daily max.
COD	<4 mg/l <10.34 lbs/day	16 mg/l 45.22 lbs/day	47.16 mg/l 118 lbs/day	20.5 mg/l 58 lbs/day	
pH	6.5	6.5	--	6.6	
NO_3-N	52.0 mg/l 134.44 lbs/day	52.0 mg/l 146.97 lbs/day	45.96 mg/l 115 lbs/day	45.29 mg/l 128 lbs/day	1,200 lbs/day
NH_3-N	1.2 mg/l 3.1 lbs/day	0.85 mg/l 2.40 lbs/day	0.24 mg/l 0.6 lbs/day	0.21 mg/l 0.6 lbs/day	
T. Kjeldahl-N	No value Interference	No Value Interference	2.04 mg/l 5.1 lbs/day	2.08 mg/l 5.9 lbs/day	115 lbs/day
T-PO_4-P	2.0 mg/l 5.2 lbs/day	2.2 mg/l 6.21 lbs/day	2.76 mg/l 6.9 lbs/day	2.55 mg/l 7.2 lbs/day	7.8 lbs/day
Soluble Fluoride	16.7 mg/l 43.18 lbs/day	17.6 mg/l 49.74 lbs/day	16.97 mg/l 48.6 lbs/day	17.19 mg/l 42.5 lbs/day	15 mg/l 38 lbs/day
Zirconium Unfiltered	3.13 ± 0.13 mg/l 8.09 lbs/day	3.01 ± 0.05 mg/l 8.51 lbs/day			
Zirconium Filtered	0.053 ± .002 mg/l 0.14 lbs/day		0.04 mg/l 0.1 lbs/day	0.035 mg/l 0.1 lbs/day	
T. Oils mg/l (1045 hrs) lbs/day	120 mg/l **† 310 lbs/day				25 mg/l 62.5 lbs/day
T. Oils mg/l (1100 hrs) lbs/day	<10 mg/l** <26 lbs/day				25 mg/l 62.5 lbs/day
T. Oils mg/l (Sandvik) lbs/day				1.98 mg/l 5.6 lbs/day	25 mg/l 62.5 lbs/day

*Actual flow for DOE 24-hr. composite sampling period.
**Total oils taken as grab samples.
†Surface grab (visible sheen).