

## **EXPERIENCES DURING 25 YEARS OF OZONATION FOR DIFFERENT INDUSTRIAL APPLICATIONS**

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### **INTRODUCTION**

A few years after the end of World War II, I attended the first environmental conference in London, England, under the auspices of London University. This conference was primarily concerned with identifying what methods could be used to bring the salmon back to the River Thames. Considered were biological, chemical and oxidation processes, along with electricity. Having learned about ozone and electrolysis during my earlier schooling, I was convinced that electrical power would play an important role in the struggle for pollution control.

Having been involved with industrial wastewater treatment for more than a quarter century, I would like to share the remarkable results from some of the earliest field-testing studies. I will illustrate and compare the ozone equipment used during those early tests with today's equipment, and will detail some early applications conducted with the highly unorthodox method called FLPC (Film Layer Purifying Compartment).<sup>1</sup>

### **CASE 1 - INDUSTRIAL WASTEWATER TREATMENT INSIDE OF PIPES**

In the late 1960's, California suffered through an extended drought. As the years past, and water resources dwindled, the press "discovered" that wastewater could be purified to the point where it could be reused in numerous applications. This drought, and the resulting press coverage, influenced our first 3-month field-test sponsored by the Canadian Government in Granby, Quebec. Granby was one of the most industrially diversified cities in Canada, and at that time was without a wastewater treatment facility. Since I was convinced (then as now) that treatment of industrial wastewater could be done effectively and economically in wastewater discharge pipes, the patented FLPC system was mounted in a 200 foot section of a six foot diameter pipe, which was buried in the ground.<sup>2</sup>

The first FLPC compartment was biological pretreatment where pure oxygen was fed counter current of the sprayed water with water droplets of predetermined size and water pressure. In the other three FLPC compartments we used oxygen/ozone mixture. Because this is accomplished in a closed system, the ozone concentration in the bulk waste and the air above it is in equilibrium, which facilitates almost instantaneous oxidation. Since the concentration of treated toxic depends upon the wastewater conditions, the decisive factor for the reaction velocity is the relative concentration of ozone in the treating gas, or, in relative dilution in oxygen. The reaction constant

will differ between each particular interaction of ozone and treated toxic compound, but an accurate figure can be determined through the operation of a pilot plant.

Variable dosages of ozone were used from 10 mg/L to 40 mg/L. The average flow was 378 M3/day. The cost of ozone/oxygen production was 16 KWH per pound of ozone, and 36 Kg of liquid oxygen was necessary to produce 1 Kg of ozone at a 2% concentration. Today the operating cost per pound of ozone is approximately 60% less, including preparation of pure oxygen, with ozone concentration increased from 2% to 6% by weight.

Liquid oxygen was supplied by the company Liquid Air free of charge in exchange for copies of the 300 laboratory tests conducted by Warnock Hersey International Limited. Table 1 below shows a typical laboratory report.

**Table 1    LABORATORY TEST RESULTS BY WARNOCK  
HERSEY INTERNATIONAL LIMITED    DECEMBER 14, 1970**

Q-3332 = Granby Raw Sewage / Q-3333 = FLPC ozone treated		
Constituents	Q-3332	Q-3333
pH	6.35	7.35
COD, ppm	7,920	160
Total solids, ppm	1,533	322
Cyanide, ppm	5.0	0.05
BOD, ppm	209	17
Dissolved oxygen, ppm	2.8	6.5
Coliforms. 100 mls	30,500	70

If the untreated effluent with dissolved solids of 1,533 mg/L had been chemically flocculated and had the solids been removed before FLPC treatment, the COD and BOD would undoubtedly have been even more drastically reduced. (Toxic discharges presently entering wastewater streams could greatly benefit from this system, eliminating discharge surcharges.) The low ozone concentration available at that time and the high cost of energy and oxygen prevented further pursuit of this promising FLPC application.

At that time we tried to mount UV lamps into the compartments but we found that most wastewater contains iron and manganese and soon a brownish film formed on the UV bulbs or covers, thus killing the UV spectrum.

NOTE: The principle of the patented FLPC system was borrowed in Europe and in the United States for air stripping of volatile organic contaminants. Using air instead of oxygen and ozone, the net result is a transfer of contaminants from one medium to another, such as to activated carbon.

## CASE 2 - CYANIDE REMOVAL

At the 1973 Canadian Mineral Processors Annual Meeting held in Ottawa, G.I. Mathieu, Research Scientist, presented the results of a 3-week feasibility study for the removal of cyanide and heavy metals from a wastewater stream.<sup>3</sup> The pilot plant system was installed at Ozonair laboratories in Ville St. Laurent, and used a Model H-6 unit. The system consisted of an ozone generator with a capacity of 12 gr/hr, one, two or three FLPC contact compartments, electrolysis equipped with powerstat, adjustable flow meters and pumps. This system had a capacity of 2 to 7 gallons per minute, and required approximately 30 gallons of liquid for a satisfactory test.

The first part of the investigation consisted of a preliminary analysis of the efficiency of the FLPC process for the destruction of simple and complex cyanides. Two types of (synthetic) cyanide solutions were investigated. One was prepared with sodium cyanide (NaCN), while the other was made of a mixture of cuprous cyanide ( $\text{Cu}_2(\text{CN})_2 \cdot \text{H}_2\text{O}$ ) and sodium cyanide. The former was chosen because it is the standard cyanide used in the gold cyanidation mills, while the latter was selected to simulate the reaction occurring in a gold copper mill (i.e. the formation of copper sodium cyanide complexes, such as  $\text{Na}_2\text{Cu}(\text{CN})_3$  and  $\text{Na}_3\text{Cu}(\text{CN})_4$ , from the reaction of cuprous and sodium cyanides). Two levels of CN concentration were tested with each type of solution (10 ppm and 100 ppm). The first represented the normal CN concentration of gold mill tailing pond overflow; the second approximates the order of cyanide content of the solution bled from the same type of mill.

**Table 2**      **CONDITIONS AND RESULTS OF CYANIDE REMOVAL TESTS**

Solution	Initial CN Concentration ppm	Treatment Cycle	Reagents		Contact Time* min	Results		CN destroyed lb	reagent consumption per lb of CN destroyed		Oxidation % efficiency	
			Added	Formed		CN Analysis ppm	% Reduction		O <sub>2</sub> cu ft	O <sub>3</sub> gram	***	
			Oxygen liter	Ozone gram							O <sub>2</sub>	O <sub>3</sub>
Type A NaCN	12.5	0 (0 min)	0	0	0	12.5	-	-	-	-	-	-
		1 (15 min)	150	6	0.6	2.0	84	0.0031	1678	1935	21.6	0
		2 (30 min)	300	12	1.2	1.5	88	0.0033	3172	3636	11.5	0
		3 (45 min)	450	18	1.8	1.1	91	0.0034	4589	5294	7.9	0
	105	0 (0 min)	0	0	0	105	-	-	-	-	-	-
		1 (15 min)	150	6	0.6	17.4	83	0.0263	196	228	100.0	3.1
2 (45 min)		450	18	1.8	3.3	97	0.0305	511	590	71.0	0	
	3 (75 min)	750	30	3.0	2.2	98	0.0308	834	974	43.0	0	
Type B (Na <sub>3</sub> CU (CN) <sub>4</sub> )	9.9	0 (0 min)	0	0	0	9.9	-	-	-	-	-	-
		1 (15 min)	150	6	0.6	0.6	94	0.0029	1793	2089	20.2	0
		2 (30 min)	300	12	1.2	0.3	97	0.0028	3715	4286	9.7	0
		3 (45 min)	450	18	1.8	0.5	95	0.0028	5573	6424	6.5	0
	120	0 (0 min)	0	0	0	120	-	-	-	-	-	-
		1 (15 min)	150	6	0.6	16.9	86	0.0350	172	198	100.0	4.2
2 (45 min)		450	18	1.8	3.4	97	0.0350	445	514	81.5	0	
	3 (75 min)	750	30	3.0	0.6	99.5	0.0358	726	838	50.0	0	

\* Estimated at 12 seconds per chamber per cycle.

\*\* Based on the equation:  $6\text{CN} + 4\text{O}_3 = 6\text{CO}_2 + 3\text{N}_2$

\*\*\* Assuming that all the ozone reacts with cyanide prior to oxygen and based on the equation:



Note: The "Rapid Colorimetric Solvent-Extraction Procedure" developed at the Mines Branch by D.J. Barkley and J.C. Ingles was used for these analyses.

With the FLPC ozone process, 91% to 97% of the cyanide was decomposed in less than two minutes of contact time independent of the initial CN concentration (10 ppm to 100 ppm), while the air-oxygen method developed at that time by Calgon Corporation required 25 minutes and the standard alkaline-chlorination technique takes one to two *hours*.. This limited investigation indicated that the cupric ions had no significant effect on the overall rate of cyanide oxidation, evidenced by the 98% CN destruction in 36 seconds with and without copper sulphate addition. However, the cupric ions do seem to foster a preliminary elimination of cyanide during the electrolysis stage, where 34.7% was eliminated in the presence of  $\text{CuSO}_4$ , and only 8.1% in its absence. For conditions and results, see Table 2 above.

### **CASE 3 - OXIDATION OF FERROUS SULPHATE BY OZONE AT NORANDA RESEARCH CENTER FOR INTERNATIONAL NICKEL POINTE CLAIRE, QUEBEC**

Sulphate solutions containing ferrous and ferric ions are frequently encountered in hydrometallurgical systems. Though the  $\text{Fe}^{2+} - \text{Fe}^{3+}$  Redox couple is recognized as an oxidant of medium power, its use in a sulphate system is restricted mainly because of the difficulty of oxidizing ferrous ion in strongly acidic solutions.

Experimental work carried out in this investigation may be divided into three parts: (1) Oxidation of reagent grade ferrous sulphate solutions to understand the system, (2) Oxidation of ferrous iron in a zinc-calcine leach slurry, and (3) Scale-up tests on a semi-pilot scale.

Large scale tests were conducted in an 800 liter reactor (60 cm dia. 120 cm high) provided with baffles, a cooling coil and a paddle type impeller. Ozone was produced by passing oxygen or pre-dried air through the laboratory ozonator. The flow rate of carrier gas was 10-15 liters  $\text{min}^{-1}$  and the rate of ozone production was about 6.0  $\text{gr/hr}^{-1}$  using oxygen and 3.0  $\text{g/hr}^{-1}$  using air. Ozone was introduced into the leach slurry as a gas or continuously as a supersaturated solution in water.

Further tests on a large scale were carried out at lower acid levels (0.5-1.0 g/l), corresponding to what is known as the 'knock-out stage' in electrolytic zinc plant practice. About 90 liters of 'ozone-saturated' water were added to about 600 liters of leach slurry, effecting a decrease in ferrous concentration from 125 to 25 mg/L. On the basis of ozone transferred, it was computed that about 70 g. of iron had been oxidized per gram of ozone supplied.

It can therefore be concluded that ozone is effective for oxidizing ferrous ion in sulphate media. The reaction follows zero order kinetics with respect to the concentration of ferrous iron in solution and the rate is independent of the pH between 4.0 and 0.5. This feature would enable the use of ozone for the regeneration of  $\text{Fe}^{3+}$  in acidic solutions. The passage of air through an electric discharge results in the production of nitrogen oxides which contribute towards the oxidation of ferrous iron in solution.

Oxidation of ferrous ion in a zinc calcine leach slurry can be carried out at both low and high acid levels. Some problems of corrosion were encountered at low pH's when a mild steel reactor was employed and destroyed. The efficiency of utilization of ozone was poorer at higher acidity levels (10-20 g/L) in solution. For compiled results, see Table 3 below.

**Table 3** *RESULTS OF OXIDATION EXPERIMENTS USING ZINC CALCINE LEACH SLURRIES*

Test No.	Source of O <sub>3</sub>	Conc. of O <sub>3</sub> (ppm)	Acid Concentration (pH)		Fe <sup>2+</sup> Analysis (mg/l)		Duration of Test (Min)	Rate of oxidation mg. l <sup>-1</sup> hr <sup>-1</sup>	Weight ratio of Fe <sup>2+</sup> oxidized to ozone supplied.
			Initial	Final	Initial	Final			
1	Air	130	8.9	6.0	425	258	130	80	9.0
2	Air	850	4.9	4.0	728	-0	140	310	6.3
3	Air	880	18.0	7.0	480	-0	90	307	8.3
4	Air	2200	20.0	11.0	224	-0	30	450	3.3
5	Air	190	1.0	0.5	320	-0	92	210	16.7
6	Air	350	1.0	0.5	290	-0	75	232	12.5
7	Air	880	1.0	0.5	373	-0	35	640	16.8
8	Air	880	1.0	0.5	202	-0	17	705	18.0
9	Air	1720	1.0	0.5	495	-0	19	1542	12.8
10	Oxygen	1280	1.0	0.5	525	-0	78	408	4.6
11	Oxygen	3640	1.0	0.5	480	-0	31	830	3.5

#### CASE 4 - TERTIARY TREATED WASTEWATER SUITABLE FOR SUBSURFACE REINJECTION

Early in 1977 we conducted three-week feasibility studies for THUMS (Texaco Humble Union Mogul Shell) at the Castaic Wastewater treatment plant in Los Angeles, California. The plant used activated sludge, chemical flocculation and multistage filtration, chlorination and dechlorination for wastewater treatment.

Norms for the THUMS Slope Test were: water volume = 1000 milliliters during one minute passing through a 0.45 milipore filter under four feet of head. Turbidity of the water equaled 0.8 JTU. The water needed to be Total Bacteria free to prevent clogging caused by organic slime which would serve as food for bacterial proliferation. For three years THUMS had tried different methods without success. The THUMS slope norms were 500-600 milliliters.

The experiments were conducted with an oxygen-fed ozone generator with a capacity of 28 gr/hr at 2% concentration. The contactors were dual FLPC type. The ozonized and sterilized water required a minimum of 2 hours settling in order to obtain the desirable slope test and turbidity of 0.5-0.8 JTU. Ozonation followed by diatomaceous filtering was able to deliver a quality of water to meet THUMS requirements. In fact, this system produced the best results by far during the three year test period. Table 4 shows typical results.

**Table 4 WATER TESTS - CASTAIC RECLAIMED FILTERED WATER (Treated)**  
*January 14, 1977*

Turbidity, JTU	0.8
Coliform, bact/ml	negative
C.O.D., mg/l	24.2

### **THE DEVELOPMENT OF A TOTAL SOLID-STATE GENERATOR**

When we founded a water treatment company in Montreal in 1966, we imported our ozone generators from Europe. The secondary voltage was 18,000 Volts with less than 1% ozone concentration. During the rainy season this high voltage and increased humidity created stress on the dielectric which led to numerous and continuous problems. It became obvious why the standard procedure was to always have a second generator on-site as a standby unit!

It became apparent that an alternative solution was needed, so we began an intensive research and development project dedicated to producing a new type of generator. Three years later a greatly improved generator was introduced which reduced the secondary voltage transformer from 18,000 Volts to 7,500 Volts + DC transformer + coil and inverter operating on 360 Hz. The fragile glass electrodes were replaced by ceramic electrodes made to our specifications in West Germany from titanium oxide ceramic. These electrodes had a 60% better dielectric constant than glass and were capable of withstanding 100,000 Volts. Utilizing an oxygen feed the ozone concentration was increased to 2% by weight and the power consumption was reduced from 12 KWH per pound of ozone to just 8 KWH per pound.

In 1975 the company moved its operations to the United States. For the next five years this new generator was sold to solve a variety of water purification problems, including new applications in the electronic industry treating D.I. water. In 1978, a 2,282,400 gallon per day system was installed at National Semiconductor's plant in California to treat D.I. water. Another new application introduced in the U.S. at this time was the treatment of cooling tower water. After a 5-month testing period at National Semiconductor a Model HF-90 ozone system was installed at the Jet Propulsion Laboratory in Pasadena. The results of their two-year study were published in 1979.<sup>4</sup> The Study's recommendation was to install similar systems on three cooling towers at the Kennedy Space Center in Florida, where high humidity and poor water quality had caused continuous problems. A three year test was recommended. At the successful completion of this test, the results were published<sup>5</sup> and presented at the annual International Water Conference. The report validated ozone as an effective and economical treatment method for cooling towers, even in difficult, high humidity regions.

Our first solid-state ozone generator was described at the American Water Works Association Water Reuse Symposium in 1981.<sup>6</sup> It was equipped with thyristorized circuitry that was found to be too fast for the incorporation of a safety circuitry. We therefore switch from thyristors to

transistors and incorporated a safety circuitry. Our ozone generators are of modular design and air-cooled. Some eight years ago we replaced dry air with pure oxygen generators. Our patented electrodes are fed in series instead of in parallel and deliver 6% ozone concentration which is necessary to treat industrial wastewater and highly contaminated water.

**Ozone Concentration.** The difference between our standard 6% concentration and others claiming a higher concentration is that we do not need to reduce our oxygen flow and generate less ozone since in the field both maximum ozone concentration and ozone capacity are required. As an example published data<sup>7</sup> shows that at 2% concentration the gas flow is 100%, at 6% concentration the gas flow is reduced to 33%, and at 10% concentration it is reduced to 20%, while at the same time the cooling water has to be pre-chilled to 10 degrees C (more energy). We are quite happy with our 6% concentration. As an example, at our testing on aircraft stripping wastewater for the U.S. Navy, with appropriate catalyst and two-stage treatment we have removed 3,000 ppm of phenol in less than 9 minutes.

We did not pursue an ozone concentration higher than 6% since during our R&D when we reached 9% with slight restriction of the ozone flow self-ignition started which resulted in a very nasty fire on a few occasions.

In the November/December issue of Ozone News we noticed that Trailigas had joined forces with Praxair, Inc., one of the leading gas companies which will be developing vacuum-type oxygen generator, indicating that at least one company is aware of the danger of self-ignition of oxygen/ozone at over 9% concentration when free flow may be accidentally restricted.

## REFERENCES

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