Generating Chlorine Dioxide Gas: Chlorate vs. Chlorite

By Douglas Rittmann, P.E. and Joel Tenney

This paper evaluates the effectiveness of generating chlorine dioxide gas using Eka Chemical's method of sodium chlorate/hydrogen peroxide/sulfuric acid technology as it compares to the Vulcan (Rio Linda®) chlorine gas/25 percent sodium chlorite system process at the El Paso Water Utilities' 40 mgd Canal (Umbenhauer/Robertson) Water Plant in El Paso, Texas. Since the Canal Water Plant is actually two 20 mgd facilities located side by side, it was ideal to run comparison plant trials of the two types of technologies in generating chlorine dioxide. The trial commenced on September 8, 1997 and continued through October 3, 1997.

The objectives of the trial were to compare the effectiveness of the sodium chlorate technology to the sodium chlorite technology in

- Providing reliable and durable machine performance;
- Producing chlorine dioxide gas at greater than 95 percent efficiency;
- Minimizing chlorate by-product residuals in the finish water; and
- Reducing cost of chlorine dioxide generation by at least 10 percent.

Introduction

Eka Chemicals developed a new, proprietary small scale chlorine dioxide process (SVP-Pure™) system for water treatment applications. This system does not use chlorine gas as a chemical reactant to produce chlorine dioxide (i.e., no chlorine residual is produced with the chlorine dioxide gas which should result in lower trihalomethane levels in the distribution system as compared to the chlorine gas/chlorite methods).

Although results of this study were inconclusive in this regard, past studies have shown chlorine alone used in pretreatment causes significantly higher trihalomethane formation levels. El Paso currently utilizes a chlorine and chlorite-based process of 960 lbs/day of generated chlorine dioxide gas for the 40 mgd Canal Plant (two 20-mgd plants). The stoichiometric chemistry of this process is shown in Equation 1.

Equation 1

$$NaClO_2 + \frac{1}{2}Cl_2(gas) \longrightarrow ClO_2(gas) + NaCl$$

To ensure high efficiency, chlorine is slightly overfed in chlorite systems. El Paso feeds chlorine at roughly 1.1 times stoichiometric or 0.57 lb. Cl_2/lb. of ClO_2. Table 1 shows the chemical consumption and estimated cost of El Paso's current chlorine/chlorite technology based on 100 percent conversion of chlorite to chlorine dioxide using 10 percent overfeed of chlorine.

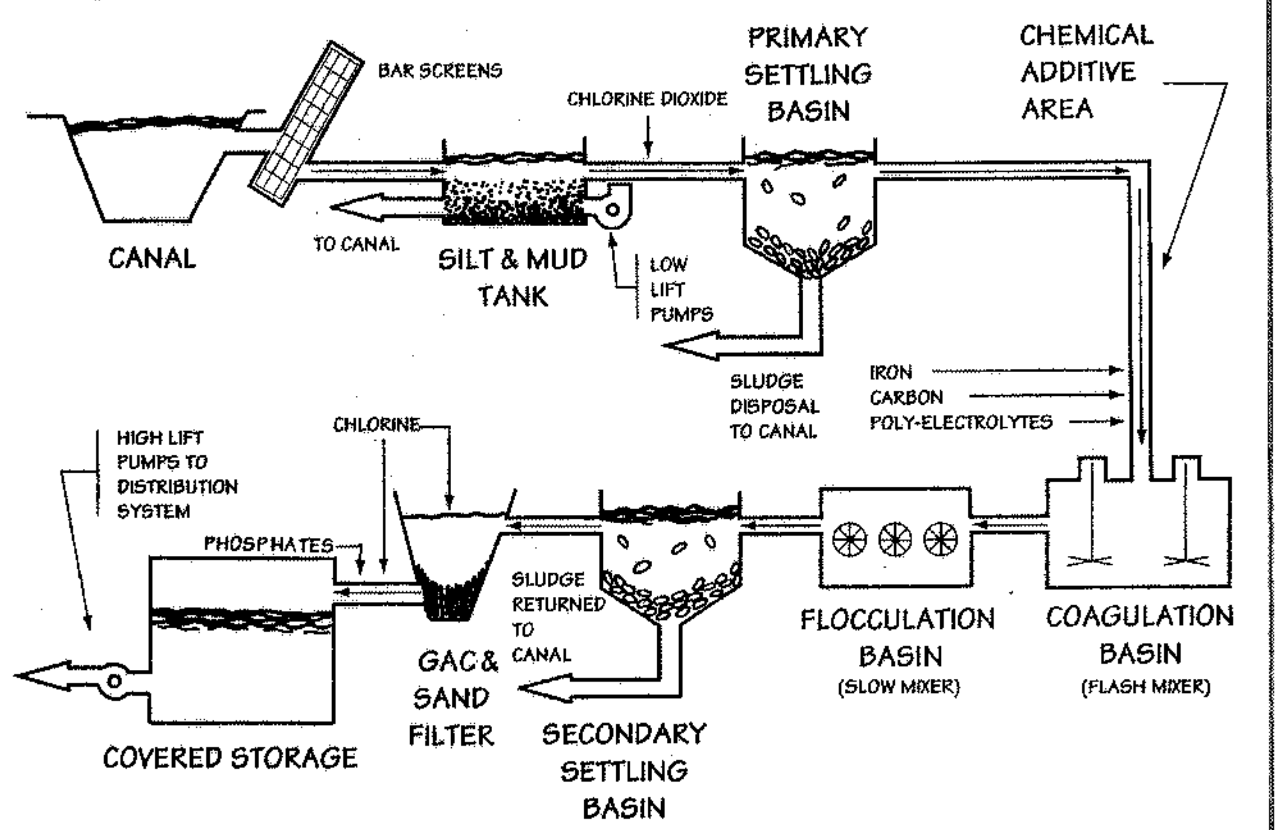
The State regulatory agency (Texas Natural Resources Conservation Commission) requires a minimum of 95 percent conversion or efficiency of the generator. At 95 percent efficiency, the cost of converting chlorine and chlorite to chlorine dioxide is $2.15 per pound of chlorine dioxide. By slightly overfeeding the chlorine gas, conversion efficiency is at its best. However, there are some probable consequences in terms of precursor reduction in the formation of trihalomethanes since a small amount of free chlorine residual is present in the chlorine dioxide/chlorite/chlorate species.

Based on the relative costs between sodium chlorate and chlorite, the chlorate process provides a lower cost alternative. El Paso wanted at least a 10 percent cost savings by using the Eka Chemicals process. In the interest of demonstrating the process attributes in the field, it was proposed that a trial be conducted.

Table 1 — Vulcan (Rio Linda®) Chlorine Dioxide Cost

Chemical	lb Consume/lb ClO_2	$/lb Chemical	$/lb ClO_2
25 Percent Chlorite Solution	5.37	$0.357	$1.92
Chlorine Gas	0.57	$0.21	$0.12
Total Cost/lb ClO_2			$2.04

Figure 1: Umbenhauer/Robertson Water Treatment Plant



Trial Results

Setup: Figure 1 shows the Canal Water Treatment Plant Flow Schematic. The plant has two-20 mgd plant trains. The plant's process is unique because it feeds a high dosage of chlorine dioxide at a rate of 2.5 ppm to 3.0 ppm to the raw Rio Grande river water. This practice is in sharp contrast with other chlorine dioxide plants that do not exceed one ppm in order to stay below the maximum contaminant level for chlorite by-product. El Paso is able to feed much higher levels of chlorine dioxide because ferrous chloride is used to convert the chlorite to harmless chloride while converting the ferrous ion to a substitute for the primary coagulant in the process. For more information, see the April 1997 article in *Water Engineering & Management* entitled "'Can You Have Your Cake and Eat It Too' with Chlorine Dioxide." This higher dosage of chlorine dioxide provides superior disinfection credit and some precursor destruction for lowering trihalomethanes potential at a rate of about 10 ppb per 1 ppm of chlorine dioxide dose to the raw water but it depends on the amount of excess chlorine in the total oxidant species.

The chlorate system was installed on the Plant 2 raw water line. Due to the high chlorine dioxide demand (480 lbs/day), two units were used. Each chlorine dioxide unit operated continuously at about a 10 lb/hour rate. The setup for the chlorite mode of operation in Plant 1 was identical except that only one unit was needed to satisfy the chlorine dioxide demand.

Objective #1 — Machine Performance

Eka Chemicals' machines availability (uptime) achieved during the two weeks of normal operation was well in excess of the 95 percent required by the El Paso Water Utility and approached 100 percent. Problems during the first two weeks of setup

Table 2: Generator Solutions Analyses

	Vulcan (Rio Linda®) Generator				Eka Chemicals Generator			
Date	ClO_2*	ClO_2^-	ClO_3^-	pH	ClO_2*	ClO_2^-	ClO_3^-	pH
10/1/97	2,000	280	70	6.0	1,000	0	46	1.7
10/1/97					1,000	0	79	1.7

*ClO_2 analyzed spectrophotometrically prior to purging with nitrogen gas
ClO_2^-, ClO_3^- analyzed by ion chromatograph after purging with nitrogen gas

Samples analyzed by Novatek

Table 3

Generator Efficiencies	Chlorite Systems	Eka Chlorate #1	Eka Chlorate #2
Maximum	99.47%	99.00%	99.00%
Minimum	90.02%	91.00%	87.50%
Average	96.51%	96.64%	96.12%

were easily addressed and posed no concern during operation. Plant staff assumed primary responsibility for operating the equipment during this time and did not encounter any undue difficulties or safety problems. The problems in the first two weeks were related to the trial installation and minor maintenance issues.

During the time of operation, only one machine issue, a loosening of the generator heads, caused a shutdown. This was caused by severe water back pressure on the units that resulted from the interim configuration for the trial period. As a result, the threads on the reactor were stripped. This was corrected by installing UHMW heads on the reactors and check valves in the unit discharge lines.

Objective #2 — Generator Solution Analysis & Efficiencies

Table 2 shows a comparison of Generator Solutions Analysis for the two systems. The Eka generator solution was more acidic and contained about the same amount of chlorate levels as the Vulcan (Rio Linda®) generator solution. However, the Eka generator solution contained no chlorite. Chlorate in the Eka solution reflects generator efficiency. The low chlorate level measured during the trial indicates high generator efficiency, greater than 95 percent. On the other hand, the presence of chlorate in the Vulcan (Rio Linda®) generator solution was not totally unexpected and is either the result of chlorate residual in the feedstock or generator inefficiency.

Table 3 shows the chlorite versus chlorate unit performance. Both processes operated efficiently maintaining average conversions of 96 percent with a range of values between 90 and 99 percent for the Vulcan (Rio Linda®) system and 87.5 to 99.0 percent for the Eka Chemical system. The reported chlorate residual in the Eka generator solution equates to a greater than 95 percent generator efficiency.

Application

The application of the chlorate chemical process to treat Rio Grande River water worked well. During the time of operation, there were no water complaints or unusual plant performance. Tables 4 and 5 summarize Plant 1 (chlorite system) and Plant 2 (chlorate system) process results. During the trial, Plant 1 treated an average of 21.5 mgd while Plant 2 treated an average of 24 mgd.

Tables 4 and 5 should be interpreted based on the range of values in each column because the flow, chemical dosages and pH data are 24 hour average readings, while the primary effluent samples for the chlorite, chlorine dioxide and total residuals data is a summary of single daily grab samples' results. Ferrous chloride is supplied as a liquid with about 12 percent iron content. FeCl dosages are calculated on a liquid to liquid basis (i.e., 64 ppm = 64 gallons/million gallons).

The Canal Plant operators normally set the raw water chlorine dioxide dosage between 2.5 ppm and 3.0 ppm. At the primary effluent, the ferrous chloride dosage is set at the rate of 3 ppm as (Fe) iron per one ppm of available chlorite/chlorine dioxide leaving the primary effluent. At full production of 20 mgd in each plant, the contact time in the sedimentation basin is 45 minutes, resulting in an average *Giardia* disinfection CT (concentration X Time) credit (.24 X 45) of 10.8 for Plant 1 and 6.3 for plant 2.

During the trial, Plant 1 chlorine dioxide dosages averaged 2.78 mg/l while Plant 2 averaged 2.34 mg/l. The total chlorine dioxide species residual averaged 2.26 mg/l in Plant 1 as compared to 2.03 mg/l in Plant 2. Since the plants depend on the conversion of ferrous to ferric at the primary effluent for its coagulant, it is likely the higher average settled water turbidities of 4.77 NTU at the filters in Plant 2 were caused by slightly underfeeding of the chlorine dioxide in Plant 2. This was because chlorite residuals were also low in Plant 2 leaving excess ferrous ion available to react with the dissolved oxygen in the water and subsequently causing higher settled water turbidity level.

Although the pH was slightly depressed in Plant 2, this does not present a problem because El Paso has high alkalinity water and with a slightly lower pH, lower trihalomethane formation in the distribution system should result. In fact, El Paso is cur-

Table 4 — Vulcan (Rio Linda®) Chlorite System

Plant 1	Primary Effluent Chlorite	Primary Effluent ClO_2	Primary Effluent Total	Settled Turbidity at Filters	Flow, mgd	FeCl Dosage, mg/l	ClO_2 Dosage, mg/l	pH at finished water
Maximum	2.47	0.64	2.48	7.0	21.52	64.04	4.58	7.50
Minimum	1.49	0	1.78	2.0	11.17	35.81	2.42	7.30
Average	2.03	0.24	2.26	3.39	19.86	46.09	2.78	7.42

Table 5

Eka Chemicals' Chlorate System

Plant 2	Primary Effluent Chlorite	Primary Effluent ClO_2	Primary Effluent Total	Settled Turbidity at Filters	Flow, mgd	FeCl Dosage, mg/l	ClO_2 Dosage, mg/l	pH at finished water
Maximum	2.44	0.46	2.82	10.6	24.04	102	2.82	7.40
Minimum	1.17	0	1.23	1.4	7.59	24	1.24	7.20
Average	1.89	0.14	2.03	4.77	20.5	39	2.34	7.30

rently considering lowering the pH during treatment with acid to increase removal of total organic carbon in order to comply with future Stage 2 disinfection by-products rule of 40 ppb TTHMs as proposed by USEPA. During 1997, the Canal Plant averaged 60 ppb for TTHMs which is below the proposed 80 ppb Stage 1 Disinfection By-Product level but El Paso must consider other treatment options such as acid/caustic addition or deeper granular activated carbon filters to comply with Stage 2 requirements.

Objective #3 — Minimizing Chlorate Levels

With the chlorite-based system [Vulcan (Rio Linda®)], El Paso must depend on a ferrous ion addition to eliminate the excess chlorite but cannot eliminate the chlorates available either from the stock 25 percent sodium chlorite solution or from possible inefficiencies of the generator. With the chlorate-based system, El Paso must depend on the efficiency of the generator to minimize chlorate levels and the ferrous ion to eliminate the excess chlorite after chlorine dioxide reacts with the raw water. However, both systems are required by TNRCC to generate chlorine dioxide gas at a minimum of 95 percent efficiency.

The intent of the efficiency requirement by the TNRCC regulation is to maximize disinfection capability but with high dosage chlorine dioxide applications in combination with ferrous ion, the main concern by the operator should be the actual chlorine dioxide and chlorite residuals present at the primary effluent (i.e., some excess chlorite from inefficiency by the generator will be eliminated by the ferrous to ferric ion reaction).

When El Paso converted a few years ago from normal chlorine dioxide dosages (1.0–1.4ppm) with ferric sulfate coagulant to high dosage chlorine dioxide with ferrous chloride, plant effluent total oxidant levels were significantly reduced. Therefore, in El Paso's case, the reasons for maximizing efficiency of chlorine dioxide generation is not only compliance with TNRCC regulations and obtaining maximum disinfection credit but to have increased THM precursor destruction and reduction of cost. In Table 6, a comparison of chlorite and chlorate levels are presented from samples taken at each plant effluent and within the distribution system that is a blend of both plants effluent. Samples were analyzed by Novatek.

Table 6 results show that the Plant 1 average chlorite level was higher than Plant 2 because of the slight underfeed of ferrous ion that resulted in improved settled water turbidity but with the consequence of 0.16 mg/l of chlorites leaving the plant. The distribution system sample's average was negligible at 0.019 mg/l because of the lower Plant 2 chlorite readings. The lower Plant 2 chlorite level was likely due to the slight underfeed of chlorine dioxide causing a slightly higher average settled water turbidity level but with the benefit of the lower chlorite level leaving the plant. The chlorate levels for both plants were very similar with the exception of one spike reading of 0.584 ppm from Plant 2 that raised the average chlorate level for that plant. Both plants were able to consistently comply with current disinfection by-products regulations for total oxidants.

Objective #4 — Reducing Cost of Chlorine Dioxide Generation By At Least 10 Percent

The first plant scale competitive bid between the two technologies, chlorite and chlorate, was received on December 30, 1997 in El Paso, Texas. The evaluative cost of generating chlorine dioxide gas from the chlorite suppliers was based on stoichiometric chemistry as presented in Table 1 and the current cost of 25 percent sodium chlorite, \$0.357/liquid pound of chlorite solution, multiplied by 5.71 to determine the cost of a pound of chlorine dioxide including chlorine cost. The Eka Chemicals system was prequalified for generating chlorine dioxide using its proprietary generator based on plant trial results.

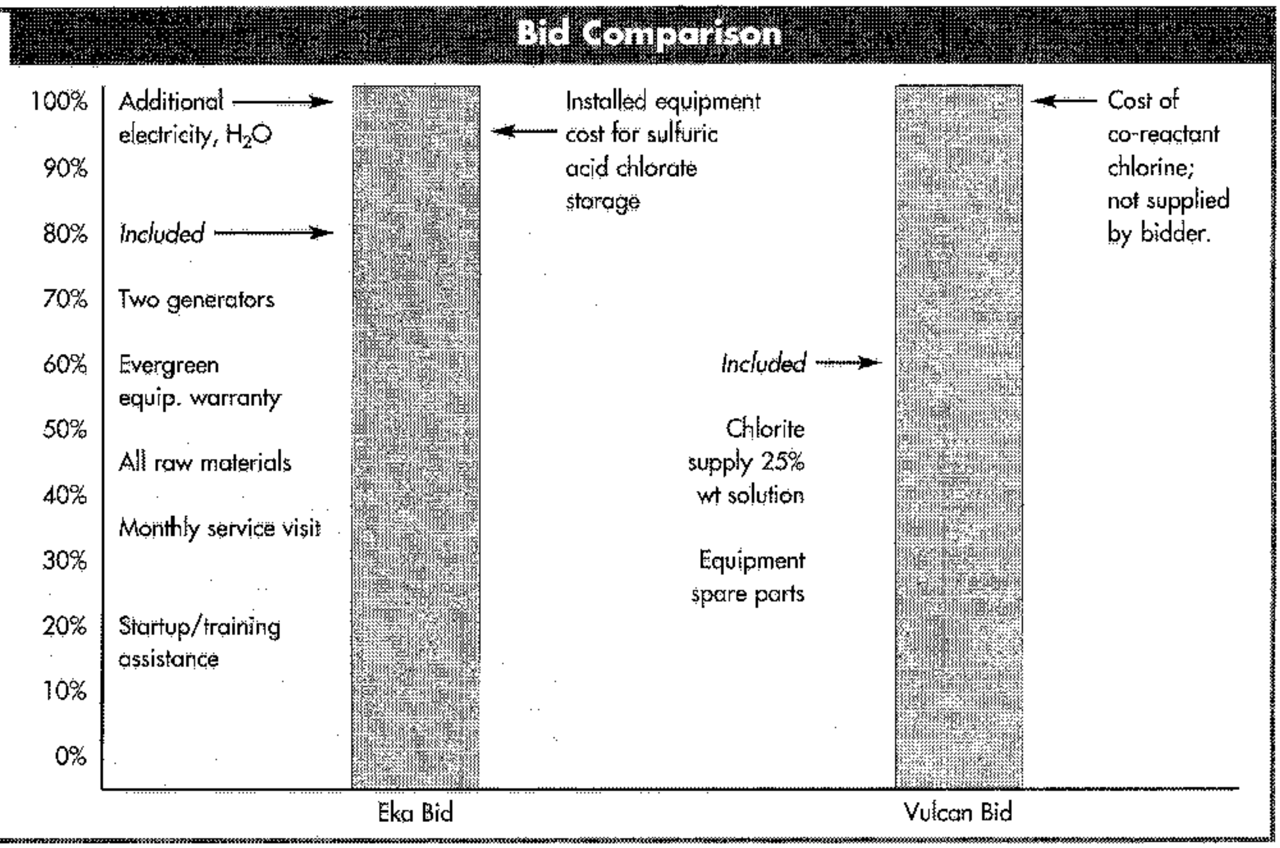
The results of the bids were \$1.82 per pound of chlorine dioxide for

Table 6

Comparison of Plants' Effluents and Distribution Samples

	Chlorite Level, mg/l			Chlorate Level, mg/l		
Location	*Maximum*	*Minimum*	*Average*	*Maximum*	*Minimum*	*Average*
Plant 1	0.391	ND	0.16	0.284	0.225	0.250
Plant 2	0.005	ND	0.001	0.584	0.226	0.349
Distribution	0.146	ND	0.019	0.411	0.176	0.273

Figure 2



Vulcan as compared to $1.84 per pound of evaluative cost of chlorine dioxide. Likely, the competition from Eka Chemicals caused Vulcan to lower their price from $.357 per liquid pound sodium chlorite to $0.319 per liquid pound, a 12 percent reduction. These bids represented a 12 percent and 11 percent reduction in costs to El Paso (a savings of roughly $22,000 annually in operating costs). The Eka Chemicals bid included an additional charge per pound to cover the costs of new storage tanks and additional electricity and water use by the process machines. Figure 2 shows the scope of the two bids and the percent of total cost represented by components/service offered.

Eka Chemicals was unsuccessful with their first public water utility bid. Since El Paso had already invested in chlorite equipment/storage, the new chlorite bid was not penalized as was the Eka bid. In any event, the introduction of a new chlorine dioxide technology has increased competition in the marketplace, as evident from the savings achieved at El Paso. This will benefit all consumers in the form of lower costs and increased service.

Conclusions

The following conclusions can be made with reasonable certainty:

1. *The El Paso trial* was successful in demonstrating the Eka Chemicals' SVP-Pure™ process. Once some of the installation issues were overcome, the units ran without incident.

2. *The Vulcan (Rio Linda®) and Eka Chemicals generators* worked equally well in efficiency at 96 percent.

3. *The Vulcan (Rio Linda®) and Eka Chemicals generators* worked well in minimizing chlorate levels.

4. *Both Plant effluents* were able to comply with total oxidant level regulations.

5. *The Eka Chemicals Generator* produces chlorite free and chlorine free chlorine dioxide that may be beneficial in further reduction of trihalomethane levels.

6. *The residual acid* from the Eka Chemicals system did not adversely affect the El Paso's water process but may result in further reduction of trihalomethane levels.

7. *The settled water turbidities* at the filters were slightly higher in the Eka Chemicals system attributed to the slight underfeeding of chlorine dioxide rather than any difference in system chemistry.

8. *The introduction of chlorate-based technologies* for generating chlorine dioxide may change the basis for the evaluation of chlorine dioxide bids to an on-site analyzed cost of chlorine dioxide.

Recommendations

- El Paso should install on-line chlorine dioxide analyzers in order to optimize chlorine dioxide dosages and as a means to determine the cost of generating chlorine dioxide.

- The evaluation of future bids should be based on an on-site generated cost.

- The cost benefits of generating chlorine free chlorine dioxide should be determined precisely in order to give it appropriate credit in the bidder's evaluative cost of generating chlorine dioxide.

- The potential impact on lower TTHMs from lower pH water and chlorine-free chlorine dioxide solution from Eka Chemicals' SVP-Pure™ System should be compared to the existing Vulcan (Rio Linda®) chlorite-based system.

About the Authors:
Douglas Rittmann, P.E., is water systems division manager for El Paso Water Utilities and a doctoral candidate in the Environmental Science & Engineering program at the University of Texas at El Paso.

Joel Tinney is senior applications engineer for Eka Chemicals.