

ILLINOIS POLLUTION CONTROL BOARD  
March 6, 1975

IN THE MATTER OF: )  
 )  
PROPOSED AMENDMENTS TO RULES ) R73-15  
203 AND 408 OF THE ILLINOIS )  
WATER POLLUTION CONTROL )  
REGULATIONS )

OPINION AND ORDER OF THE BOARD (by Mr. Henss):

Ozark-Mahoning Company and Minerva Oil Company filed a joint proposal seeking changes in Rules 203 and 408 of the Water Pollution Control Regulations as those Rules pertain to fluoride. The proposal was to relax the standard for mining companies by adding the sentence which has been underlined.

Rule 203(f) Water Quality Standards - General Standards

<u>Constituent</u>	<u>Storet Number</u>	<u>Concentration (mg/l)</u>
Fluoride	00950	1.4*

\*Except that fluoride derived from mining and concentrating the mineral fluorspar (CaF<sub>2</sub>) shall not exceed 15 mg/l.

Rule 408(a) Effluent Standards - Additional Contaminants

<u>Constituent</u>	<u>Storet Number</u>	<u>Concentration (mg/l)</u>
Fluoride (total)	00951	2.5*

\*Except that fluoride derived from mining and concentrating the mineral fluorspar (CaF<sub>2</sub>) shall not exceed 15 mg/l.

The proposed amendments and a statement of reasons supporting the proposal were published in Board Newsletter #78, dated December 29, 1973. Public hearings on the proposal were held in Elizabethtown on March 29, 1974 and in Chicago on April 19, 1974. Pursuant to its Petition to Intervene, Olin Corporation was designated a party in interest and granted leave to participate in the hearings. Other participants included the U. S. Environmental Protection Agency, the Illinois Environmental Protection Agency, Allied Chemical Company and private citizens.

The existing effluent limitation of 2.5 mg/l for fluoride was adopted by the Board on January 9, 1972 following extensive public hearings through the State. In setting this limitation the Board stated:

"Fluoride. Our initial proposal for a fluoride effluent standard was 1.0 mg/l. This was somewhat tighter than the water quality standards we later proposed (1.4) for both aquatic life and public water supply, and it posed problems for municipal treatment plants whose influent has been deliberately dosed with as much as 1.0 mg/l of fluoride for dental purposes. Patterson reported that 1.0 mg/l was achievable only through relative exotic and costly methods, such as ion exchange, and that 10.0 mg/l was a more appropriate standard to achieve by ordinary precipitation. Weston and Dodge both said, however, that 1.0 was readily achievable, Weston specifying the use of alum at cost less than those for achieving most of the metals concentrations here proposed. The most specific information in the record came from Olin, which reports that its fertilizer works at Joliet consistently reduces fluoride concentrations by standard treatment from an influent of 15 mg/l to an effluent of 2.5, but that other ions present prevent reduction as low as 1.0.

We have accepted Olin's figure of 2.5 mg/l, in recognition of the difficulties encountered in going lower and of the likelihood of dilution in many instances to achieve a relatively lenient stream quality standard."

A water quality standard of 1.4 mg/l fluoride was adopted on March 7, 1972, again following extensive public hearings throughout the State. On the fluoride water quality standard the Board stated:

"Fluoride. Fluoride can delay the hatching of fish eggs and has been reported by McKee and Wolf to kill trout at concentrations ranging from 2.3 to 7.2 mg/l. They recommend a standard of 1.5 mg/l. The figure of 1.4, here repeated from the May 12 draft, is in line with that recommendation and also should assure a potable supply."

Both proponents in this matter are actively engaged in the mining and processing of fluorspar (also known as fluorite) for various industrial uses. Operating in Pope and Hardin Counties in Southern Illinois, Proponents extract the fluorspar from bedded and vertical vein deposits 350 to 850 feet below surface. They are the only fluorspar producers in Illinois and their combined production accounts for 80% of the entire amount produced in the United States. Ozark-Mahoning processes about 17,000 tons of crude ore per month at its Rosiclare mill. Minerva processes from 900 to 1300 tons of crude ore per month, from which about 157 tons of fluorspar concentrate, 20 tons of zinc concentrate and 30 tons of barite ( $BaSO_4$ ) are extracted.

During the concentrating processes, part of the fluorspar in the crude ore is dissolved and discharged in the mill effluent. Some fluoride is also contained in the discharges from the fluorspar mines.

The two counties in which the fluorspar industries operate are described as two of the smallest and most sparsely populated counties in Illinois. The 1970 Census showed that Hardin County had 4914 people on 183 square miles while Pope County had 3,857 people on 381 square miles. Ozark-Mahoning employs 220 persons directly and another 55 to 60 on contract. Minerva employs 210 persons directly and 40 persons indirectly. The majority of the workers reside in either Hardin or Pope County. The only other industries in the two-county area are quarrying, farming and cattle raising. Proponents state that the economy of these two counties is largely dependent upon the fluorspar industry as are the users of the fluorspar product insofar as total domestic production is concerned.

Fluoride-bearing effluent from proponent's mines and mills is discharged to receiving streams which vary from intermittent drainage ditches or creeks to flowing rivers as follows:

OZARK-MAHONING COMPANY

Parkinson Mine	- To Big Grand Pierre Creek to Ohio River.
Barnett Mine	- To Big Grand Pierre Creek to Ohio River.
Barnett Air Shaft	- To unnamed creek to Little Grand Pierre Creek to Big Grand Pierre Creek to Ohio River.
Oxford Mine #7	- To unnamed creek to Duck Creek to Rock Creek to Harris Creek to Saline River to Ohio River.
Knight Mine	- To unnamed creek to Mud Creek to Three Mile Creek to Ohio River.
W. L. Davis Mine #1	- To Davis Branch to Big Sinks to Ohio River (possibly)*
Rosiclare Lead and Fluorspar Mine	- To Willow Creek to Ohio River
Rosiclare Flotation Plant	- To settling pond to Ohio River
North Green Mine**	- To Sheridan Branch to Haney Creek to Ohio River
West Green Mine**	- To Sheridan Branch to Haney Creek to Ohio River

MINERVA OIL COMPANY

Mine #1	- To Running Bear Creek to Rock Creek to Saline River.
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MINERVA OIL COMPANY (continued)

Mill #1	- To Rock Creek to Saline River.
Crystal Mill	- To unnamed creek (sometimes called Davis Creek) to Big Sinks to Ohio River* (possibly)
Gaskins Mine	- To Big Grand Pierre Creek to Ohio River
Tucker Hill Area	- To unnamed creek to unnamed creek to Rock Creek to Harris Creek to Saline River to Ohio River.
Spivey Mine	- To Goose Creek to Harris Creek to Saline River to Ohio River.
Deardorff Mine	- No discharge***

\*The Big Sinks, a natural sinkhole, drains periodically to an unknown receiving stream. It is believed that water drains from Big Sinks through an underground stream to the Ohio River, although dye tests have been unsuccessful in confirming the location of the ultimate receiving stream.

\*\*Initial information showed that both the North and West Green Mines were not consistently discharging water. When operating conditions required the pumping of water from these mines, it was done on an intermittent basis only (1 to 4 hours per day) and the mine water was discharged to the streams shown. New information shows that these mines are now discharging water consistently at a combined rate of 100,800 gpd.

\*\*\*Mine water from this mine flows underground through depleted excavations to Ozark-Mahoning's W. L. Davis Mine. Such flow is minimal.

The other industrial firms participating in this matter have fluoride problems significantly different from those of the mining companies and from each other. At its Blockson Works in Joliet, Olin imports calcium phosphate rock, soda ash and sulfuric acid which are used to manufacture sodium phosphate. Fluoride-based products are also produced at the Blockson Works through the reaction of sulfuric acid and fluorspar to form hydrofluoric acid. The hydrofluoric acid is then reacted with other materials to form the desired fluoride-based final product. Fluoride-bearing effluent from Olin's Blockson Works is discharged to the Des Plaines River.

Allied Chemical operates a facility for the production of uranium hexafluoride (UF<sub>6</sub>), sulfur hexafluoride (SF<sub>6</sub>), fluorene, antimony pentafluoride and iodine pentafluoride in Metropolis, Illinois. Allied's liquid discharge, which consists of spent ammonium sulfate solution, sulfide liquors, hydrofluoric acid solution, spent potassium hydroxide solution and uranium recovery leach liquors, flows to the Ohio River through two industrial ditches.

Corporate positions on these matters vary as widely as do the processes in which the fluoride bearing wastes are generated. As earlier noted, Ozark-Mahoning and Minerva propose to amend the standards only as those standards apply to the fluorspar industry. Olin's position was one of disagreement with Ozark-Mahoning and Minerva over the proposed changes in Rule 408. Olin proposes to change Rule 408 to allow a fluoride effluent concentration of 10 mg/l for all industries. Olin took no position on the proposed change in Rule 203.

Allied first contended that the effluent standard should be revised to allow 15 mg/l fluoride based on an average of 24 hour composite analysis for 30 consecutive days and 30 mg/l maximum for any one 24 hour composite. Allied took no position on the proposed revision of Rule 203. Neither the U. S. environmental Protection Agency nor the Illinois Environmental Protection Agency took a position on the proposed changes prior to the public hearings. Their post hearing comments will be discussed elsewhere in this Opinion. Of the two Agencies, only the U. S. EPA chose to present any testimony.

Fluorides are widely distributed in the earth's crust, occurring in both igneous and sedimentary rocks. Among the more common fluoride minerals are fluorspar ( $\text{CaF}_2$ ), villiaumite ( $\text{NaF}$ ), cryolite ( $\text{Na}_3\text{AlF}_6$ ) and fluorapatite [ $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$ ]. Fluorides in high concentrations are not a common constituent of natural surface waters but they may be prevalent in detrimental concentrations in ground waters.

Small concentrations of fluoride (0.6 mg/l to 1.7 mg/l) in drinking water have been shown to effectively reduce the prevalence of dental carries while excessive amounts cause effects in humans varying from mottled teeth to death. When fluoride is 2.5 mg/l 75% to 80% of children have mottled teeth. In drinking water, fluoride of 180 mg/l is toxic and 2000 mg/l is lethal to man.

Solubility of a fluoride varies according to the nature, pH and temperature of the solvent, cationic partner and prevalence of other chemical constituents in the solvent. The two most discussed fluoride compounds during these proceedings, sodium fluoride and calcium fluoride, vary significantly in their solubility. The solubility of calcium fluoride at 18° C. (64.4° F) is 16 ppm (about 8 ppm fluoride ion) whereas the solubility of sodium fluoride is about 19,000 ppm. This means that sodium fluoride is inherently more soluble in water than is calcium fluoride.

Neither Ozark-Mahoning nor Minerva discharges any effluent that approaches the proposed effluent limit of 15 mg/l fluoride. Discharges from the mines and mills operated by these two companies are less than 5 mg/l, as shown below, with a single exception of

the discharge from the Rosiclare flotation plant settling pond.

OZARK-MAHONING

Parkinson Mine - 40 gpm   Barnett Mine - 50 gpm   Barnett Air Shaft - 40 gpm

	<u>Fluoride, mg/l</u>
Big Grand Pierre above discharge	0.28
Parkinson discharge to Big Grand Pierre	1.40
Barnett Mine discharge to Big Grand Pierre	2.40
Big Grand Pierre below Parkinson and Barnett	0.30
Barnett air shaft discharge to unnamed creek	3.10
Unnamed creek at confluence with Little Grand Pierre	0.50
Little Grand Pierre above confluence with unnamed creek	0.25
Little Grand Pierre below confluence with unnamed creek	0.40
Big Grand Pierre below all discharges	0.28

Oxford Mine #7 - 10 gpm

Mine discharge to unnamed creek	2.20
Unnamed creek at confluence with Duck Creek	0.25
Duck Creek above confluence with unnamed creek	1.50
Duck Creek below confluence with unnamed creek	1.00
Duck Creek above confluence with Rock Creek	0.97
Rock Creek above confluence with Duck Creek	0.25
Rock Creek below confluence with Duck Creek	0.63

Knight Mine - 90 gpm

Knight discharge to unnamed creek	1.40
Unnamed creek above confluence with Mud Creek	0.75
Mud Creek above confluence with unnamed creek	0.25
Mud Creek below confluence with unnamed creek	0.25

W. L. Davis Mine #1 - 1200 gpm

Mine discharge to unnamed creek	1.4
Unnamed creek above entry to Big Sinks	1.2

Rosiclare Lead and Fluorspar Mine - 20 gpm

Mine discharge to Willow Creek	1.3
Willow Creek above confluence with Ohio River	1.4

Rosiclare Flotation Plant - 650 gpm

Plant discharge to settling pond	--
Settling pond discharge to Ohio River	10.0

MINERVA

Fluoride, mg/l

Mine #1 and Mill - 368 gpm

#3 pond discharge to Rock Creek	4.5 (avg.)
Rock Creek above #3 pond discharge	0.6 (avg.)
Rock Creek below #3 pond discharge	2.5 (avg.)
Harris Creek below confluence with Rock Creek	0.45
Saline River above confluence with Harris Creek	0.40
Saline River at confluence with Harris Creek	0.47

Crystal Mill - 52 gpm

Heavy-media-separation tails	3.62 (avg.)
Unnamed creek above HMS tails	1.34 (avg.)
Big Sinks	1.51 (avg.)

Tucker Hill Area - 150 gpm

Churn Drill Hole, underground water	3.02 (avg.)
Unnamed creek upstream	No flow
Unnamed creek downstream	1.14

Gaskins Mine - 875 gpm

Gaskins Shaft	1.58 (avg.)
Big Grand Pierre Creek above discharge	0.39 (avg.)
Big Grand Pierre Creek below discharge	0.50 (avg.)

Spivey Mine - 80 gpm

Spivey Shaft	2.75 (avg.)
Goose Creek above discharge	0.51 (avg.)
Goose Creek below discharge	0.66 (avg.)

C. B. Rash, Ozark-Mahoning's Superintendent of Milling, explained that the proposed 15 mg/l effluent limitation was necessary as a "safeguard" in the event recycling of effluent was imposed upon the industry (R. 41). Ozark-Mahoning's plant in Colorado attempted a waste water recycling effort when the Colorado Department of Public Health requested an effort to achieve "zero flow". Although "zero flow" was not achieved, the effort resulted in the recycling of 80% of the waste water--but at a price. This price was an increase in fluoride concentration to 32 ppm.

When the Board set the effluent standard at 2.5 mg/l it relied heavily upon the testimony of an Olin employee, Emil Stoltz, regarding

the technology available to reduce fluoride in waste water. Stoltz had testified that while Olin had not been able to "obtain it in our specific effluent" they did have the technology to "get down to 2 to 2 1/2 mg/l."

Stoltz testified in the current proceedings that he had meant to inform the Board that this level of fluoride reduction was only a technical feasibility based on laboratory studies made at the corporation's research headquarters in New Haven, Connecticut. This research was primarily based on a lime treatment process which Olin has not used at its Blockson Works. Stoltz testified that, based on the research program, he now believes that Olin could reduce the fluoride in waste water from 15 mg/l to 2.5 mg/l. Blockson Works waste water currently contains about 20 mg/l fluoride before treatment (R. 224).

At this point, it is necessary to review the health related information about fluorides in order to provide a balance to the later discussion on feasibility and economic reasonableness of fluoride treatment.

In setting a 1.4 mg/l fluoride water quality standard, the Board cited a report by McKee and Wolf (McKee, J. E., and Wolf, H. W., Water Quality Criteria, California State Water Resources Control Board, Second Edition, 1963) showing that fluoride can delay the hatching of fish eggs and that concentrations ranging from 2.3 to 7.2 mg/l can kill trout. These references, p. 191 of the McKee-Wolf report, also show that in 15 studies the majority involved the use of sodium fluoride and none of the studies is shown to have involved calcium fluoride.

Under Sodium Fluoride, McKee-Wolf cite research showing the following effects of sodium fluoride on certain aquatic bacteria, algae and small crustaceans:

<u>Species</u>	<u>Results</u>
Daphnia (an order of crustaceans which includes water fleas, found everywhere in fresh waters)	Threshold of NaF at 23° C. was found to be 270 mg/l for a 2 day exposure.
Scenedesmus (a fresh water algae, most common and best known of all algae, found almost anywhere algae grows)	Threshold of toxic effect was 95 mg/l during 4 days at 24° C.
Microregina (A single cell protozoan often found in fresh water)	Threshold of toxic effect was 226 mg/l during 4 days at 24° C.



<u>Species</u>	<u>Results</u>
Escherichia coli (a bacteria found abundantly in vertebrate intestine)	Threshold of toxic effect was 180 mg/l during 4 days at 27° C.
Free-living protozoa and fresh water rotifers	Survived and reproduced in water containing 1000 mg/l but were killed at 1700 mg/l.

This information tends to show that low concentrations of sodium fluoride probably would not present any significant toxicological difficulties for at least some of the more common lower aquatic organisms expected to inhabit Illinois streams. Based on research reported in McKee-Wolf, the same is not true for higher aquatic organisms. This research reported the following effects of sodium fluoride on fish:

<u>Concentration, mg/l</u>	<u>Type Fish</u>	<u>Effect</u>
2.3 to 7.3	Trout	TL <sub>m</sub> at 18° C. in soft water
2.6 to 6.0	Trout	TL <sub>m</sub> at 13° C. in soft water
2.7 to 4.7	Trout	TL <sub>m</sub>
5.9 to 7.5	Trout	TL <sub>m</sub> at 7.5° C. in soft water

Thus, it would appear that some lower aquatic organisms are able to tolerate sodium fluoride concentrations on the order of 100 times that tolerated by trout. Although time of exposure for determining TL<sub>m</sub> is usually specified, this parameter was not provided for the data above, making comparison of results impracticable. Reasons for these phenomenal differences in survivability (for example, osmotic capabilities of membranes of lower aquatic forms vs. higher aquatic forms, significant physiological differences, etc.) were not stated.

In this proceeding, expert testimony indicates that sodium fluoride concentrations in natural waters should be minimal in comparison to concentrations of calcium fluoride. Dr. W. F. Sigler, head of the Wildlife Science Department at Utah State University, testified that all research conducted in the U. S. on fish fluorosis "was done by me and under my direction". Dr. Sigler noted that while small amounts of sodium fluoride might exist, larger amounts do not exist naturally because it dissociates to form calcium fluoride.

A number of opinions on the relative toxicities of sodium and calcium fluoride were aired during the hearings. C. B. Rash testified that his opinion of available research was that sodium

fluoride "would be more toxic than calcium fluoride even at the same concentration, because there is indication that the calcium present with the fluoride ion reduces the toxicity" (R. 45).

Dr. Sigler first testified that sodium fluoride and calcium fluoride have equal toxicities at equal concentrations. (R. 120) Admittedly not a chemist, Dr. Sigler later qualified this statement by testifying that the toxicities would be equal except when other positive ions were present (R. 155). Then later, Dr. Sigler testified that calcium fluoride would be the less toxic of the two fluorides because "calcium and the fluoride have an affinity for each other and reduces the toxicity" (R. 206). Dr. Sigler indicated his preference to let Franklin Davis of the Colorado School of Mines Research Institute answer the questions relating to the chemistry of fluorides. When called upon, Davis testified that he could not "answer that with the proper credentials" because he was not a toxicologist (R. 164).

Significant testimony on fluoride toxicity was produced by Dr. Leonard Krause of Olin Chemical Company. Dr. Krause testified that fluoride entering the system of any living organism will combine with the most prevalent tissue around it, usually tissue containing calcium such as cartilage or bony tissue. Such a combination is known as fluorosis. Fluoride interferes with enzyme systems at the cellular level and interferes with the oxygen uptake in organisms by some mechanism that toxicologists don't yet understand (R. 322).

Fluoride taken into a body in the form of calcium fluoride tends to be excreted almost exclusively as calcium fluoride. This occurs, according to Dr. Krause, because very little, if any, of the fluoride will combine with the body calcium since sufficient calcium is already available for combining with the fluoride.

Dr. Krause testified that his research work involving humans showed that 14 mg/l of calcium fluoride was not toxic to humans. He did not think a toxic level of calcium fluoride in solution could be reached because it would be precipitating out. Dr. Krause stated that he would not hesitate to drink water containing 14 mg/l of calcium fluoride but would never put the same amount of sodium fluoride into his body (R. 332). Fluoride in water containing sodium fluoride would not be excreted as would the calcium fluoride. It would be available to bony tissues and kidneys.

Another of the body elements that could be affected by the ingestion of calcium fluoride is potassium, an essential element in nerve tissues. At first Dr. Krause stated unequivocally that potassium in the body would not be replaced by the calcium in

calcium fluoride because of the tight chemical bond found in calcium fluoride (R. 335). He later acknowledged that such a replacement possibility did exist (R. 342) although the fluoride itself is more available to cartilaginous and bony tissue than for nerve tissue (R. 351).

Table 6-5 of the McKee-Wolf report shows various levels of fluoride concentrations that caused mottled teeth. In the range from 0.2 to 1.0 mg/l fluoride the mottling is mild with a concentration of 1.0 mg/l listed as the "threshold for mottling". One study reveals a mild to moderate degree of mottling from 1.0 to 2.0 mg/l fluoride. At 6.0 mg/l the references reported pitting and chipping of teeth and that 100% of children had mottled teeth.

E. F. Carter, Jr., Rosiclare postmaster, testified that he knew of no mottling of teeth in the Pope-Hardin County area caused by the discharges of Ozark-Mahoning or Minerva. W. W. Fowler, Ozark-Mahoning Vice President and General Manager, testified that he knew of no adverse effects, including mottling of teeth, that had been suffered by any of his employees. He added that miners have drunk water from the mine seams and walls for a number of years. The highest fluoride concentration in such water was found to be 2.5 mg/l. C. B. Rash also testified that he had observed no ill effects or mottling of teeth in the area.

Rash testified that several farmers in the area depend on the mine discharge water as a source of water for their livestock. The farmers had informed Rash that they had never observed any ill effects in their cattle as a result of drinking the mine discharge water.

Proponents submitted a letter from Truman Louderbach, a Research Biologist at the Colorado School of Mines Research Institute (CSMRI), reporting on results of bioassay testing conducted at CSMRI at the request of Ozark-Mahoning Company (Petitioner's Exhibit 4). For the test, samples were drawn from the tailings dam effluent of Ozark-Mahoning's Cowdrey, Colorado operation and from Pinkham Creek above the confluence with the tailings dam effluent. These samples had the following properties:

	<u>Tailings Dam Effluent</u>	<u>Pinkham Creek</u>
Temperature	7° C. (44.6° F.)	6.5° C. (43.7° F.)
pH	7.6	7.5
D.O., ppm	8.3	7.0
F <sup>-</sup> , ppm	32	2.6

Six-month-old fingerling rainbow trout were acclimatized for 10 days in Pinkham Creek water at 15° C. + 2° (59° F.) with a dissolved oxygen concentration above 7 ppm. Following the acclimatization the trout were subjected to testing using various mixtures of Pinkham Creek water and tailings dam effluent up to 100% tailings dam effluent. The tests showed a 100% survival of trout for 96 hours in all mixtures including the undiluted tailings dam effluent. No evidence of distress in the behavior of fish specimens was observed.

Also submitted by proponents was a report by CSMRI's Senior Research Biologist, Dr. Gary D. Boss, in which Boss summarized his findings on fluoride toxicity based on published reports. According to the Boss report, assignment of specific toxic levels is difficult because of the following major factors:

1. Fish species, race, or strain
2. Fish size and stage of development
3. Physiological state, including age of fish
4. Level, type and solubility of fluoride and fluoride containing compounds
5. Water temperature
6. Individual biological response
7. Composition of the water, in particular the content of calcium, magnesium and chloride

Boss cites a Utah State University study (Neuhold and Sigler, 1960) conducted on carp and rainbow trout, using fluoride containing water with a calcium and magnesium content of less than 3 ppm. Results were reported as follows:

<u>Species</u>	<u>Temperature, °F.</u>	<u>TL<sub>50</sub>* at F<sup>-</sup>ion conc. (ppm)</u>
Trout	55	2.7 to 4.7
Carp	65-75	75.0 to 91.0

\*TL<sub>50</sub> - Tolerance limit at which 50% of the fish survived and is nearly equal to LD<sub>50</sub> (lethal dose) and LC<sub>50</sub> (lethal concentration)

Boss qualifies the above results by stating "Fish populations including rainbow trout flourish in Wyoming and Nevada where fluoride concentrations are 13.0 - 14.0 ppm. Yet reared trout have displayed TL<sub>50</sub>'s of about 3.0 ppm of fluoride (Sigler and Neuhold, 1972)".

The Boss report cites another study of response of rainbow trout eggs in water containing less than 3.0 ppm of calcium and magnesium under varying temperatures (Neuhold and Sigler, 1960). Reported results were as follows:

<u>Temperature, °F</u>	<u>TL<sub>50</sub>, ppm F<sup>-</sup></u>	<u>Hours</u>
46	222-273	424
55	242-261	214
60	237-281	167

These data show that fluoride toxicity increases for trout eggs with increasing temperature.

Information was also reported on efforts to determine the effect of chloride concentration on rainbow trout (Neuhold and Sigler, 1962). In water containing measured amounts of fluoride and chloride ions, the following results were obtained:

<u>F<sup>-</sup> ion, ppm</u>	<u>Cl<sup>-</sup> ion, ppm</u>	
	0	9
	<u>(Deaths)</u>	
0	0	0
4	0	0
7	1	0
13	6	1
25	10	1

Boss states that such evidence indicates that the presence of either calcium, magnesium or chloride ion decreases the toxic level of fish to the fluoride ion. While admitting that the effect of the chloride ion is conditional, Boss asserts that "the weight of the experimental evidence supports the contention that fish acclimated to moderate concentrations of chloride ion have increased resistance to fluoride toxicity."

Summarizing, Boss states: "Fluoride ion has a high affinity for calcium and its presence in the water in significant amounts seems to reduce the effective concentration of calcium in the body of the fish. CaF<sub>2</sub>, however, dissociates to form so few fluoride ions that evidently only light symptoms of fluorosis are produced. Moreover, the calcium ion made available by the dissociation of CaF<sub>2</sub> would seem to provide a replacement for any calcium extracted from the body of the fish."

Boss's overall conclusion based on available information was that "in our opinion, data on fluoride toxicity are too general and vague to establish a valid toxicity level for aquatic life at this time".

As will be noted in the following table, waters used in the tests just described bear little, if any, resemblance to stream conditions applicable to the parties in this proceeding. This table provides definitive stream values in relation to various streams

receiving proponents effluent, the Des Plaines River near Olin's Blockson Works and the Ohio River near Allied's Metropolis plant:

<u>Average Stream value (1)</u>	<u>Big Grand (2) Pierre Creek, AL01</u>	<u>Saline River South Fork (3)</u>	<u>Saline (4) River, AT04</u>
ph	7.5	---	6.5
D.O.	7.9	---	8.0
Fluoride	0.6	0.3	0.4
Chloride	13	---	49
Hardness	---	160	---
	<u>Saline (5) River, AT02</u>	<u>Ohio (6) River, A08</u>	<u>Ohio (7) River, A07</u>
ph	7.6	7.9	7.8
D.O.	8.2	8.4	8.6
Fluoride	0.2	0.2	0.1
Chloride	23	100	22
Hardness	---	---	---
	<u>Ohio (8) River</u>	<u>Ohio (9) River A01</u>	<u>Ohio (10) River, A02</u>
ph	---	7.7	7.6
D.O.	---	8.6	8.7
Fluoride	0.6	0.2	0.1
Chloride	---	24	19
Hardness	160	---	---
	<u>Ohio (11) River, A06</u>	<u>Ohio (12) River, A04</u>	<u>Ohio (13) River</u>
ph	7.5	7.6	---
D.O.	7.6	7.8	---
Fluoride	0.2	0.2	0.3
Chloride	22	20	---
Hardness	---	---	178
	<u>Des Plaines (14) River, G12</u>	<u>Des Plaines (15) River, G01</u>	
ph	7.3	7.4	
D.O.	7.0	7.3	
Fluoride	0.8	0.8	
Chloride	120	165	
Hardness	320	290	

- (1) Stream identification followed by an "A" or "G" identification number (i.e., AL01, G12) represents data taken from Illinois EPA Water Quality Network, Summary of Data, 1972. Stream identification without an "A" or "G" identification number represents data taken from Illinois EPA Public Water Supplies Data Book, 1973 (Allied Exhibit #2). Values reported in mg/l.
- (2) Below discharge from Minerva's Gaskins Mine. At or near discharges from Barnett Air Shaft, Barnett Mine and Ozark-Mahoning's Parkinson Mine.
- (3) Above fluorspar mine discharges.
- (4) Far above fluorspar mine discharges.
- (5) Mouth of River below fluorspar mine and mill discharges.
- (6) Near Shawneetown, above fluorspar mine and mill discharges.
- (7) Near Cave-In-Rock, below confluence of Saline and Ohio Rivers.
- (8) Rosiclare water intake below discharge from Ozark-Mahoning's Rosiclare Mill.
- (9) Golconda water intake below fluorspar mine and mill discharges.
- (10) Brookport below all fluorspar mine and mill discharges but above discharge from Allied plant.
- (11) Olmsted below Allied plant discharge.
- (12) Cairo water intake.
- (13) Cairo water intake.
- (14) Above discharge from Olin's Blockson Works.
- (15) Below discharge from Olin's Blockson Works.

From the record it is apparent that the determination of toxicity in this matter depends largely upon the concentration of ions in the receiving waters, particularly calcium and magnesium ions. The reports refer to the concentration of these ions as hardness. (Water hardness in the Des Plaines River near Olin's Blockson Works is about 90% calcium and 10% magnesium [R. 222]). As the above Table shows, Illinois streams are not deficient in calcium and magnesium ion concentrations.

On this basis, toxicity data submitted by Allied Chemical appear to be more pertinent to this proceeding than any other data submitted. Allied contracted Industrial Bio-Test Laboratories Inc. to conduct a 4-day static fish toxicity study using bluegill sunfish (*Lepomis macrochirus*) and channel catfish (*Ictalurus punctatus*). A test solution was prepared by using de-ionized water and measured amounts of calcium and magnesium sulfate, sodium bicarbonate and potassium chloride. Water taken from the Ohio River near Metropolis was used as a dilutant.

Sodium fluoride, calcium fluoride and hydrofluosilicic acid were added at test concentrations of 2.5, 10.0 and 20.0 ppm fluorine to separate vessels, each containing 10 specimens of each species of fish. An untreated sample containing only river water was used as a control. Water temperature was maintained at about 18° C. (64.4° F.).

In the test using sodium and calcium fluoride no fish fatalities had occurred after 96 hours exposure to the calcium fluoride test solution. One bluegill died after 24 hours exposure to the 10.0 ppm sodium fluoride solution and another died after 72 hours exposure to the 20.0 ppm sodium fluoride solution. No catfish fatalities occurred in the sodium or calcium fluoride solutions. Investigators concluded that the 96-hour TL<sub>50</sub> of both sodium and calcium fluoride for unacclimated native fish is in excess of 20 mg/l

These results are particularly important and directly relatable to Illinois streams. They again point to the importance of associating fluoride toxicity levels with calcium and magnesium concentrations in surface streams.

Another document which provides additional insight into the effect of fluoride on stream quality was submitted as Proponent's Exhibit #14. This document reports the results of a biological survey conducted by the Illinois EPA on February 6-7, 1974 to determine the condition of stream environments relative to discharges from Minerva's Gaskins Mine. The survey reveals well balanced benthic invertebrate populations both upstream and downstream from the mine discharge. (An unnamed tributary receiving effluent from the mine was reported to be "semi-polluted" with the cause appearing to be of an "organic origin"). Although fluoride concentrations are not reported in the biological survey, data reported earlier in this Opinion indicate that the fluoride water quality is being met and this receiving stream is adequately protected.

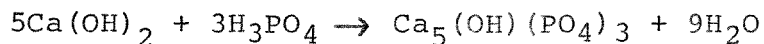
Turning now to the question of economic reasonableness and technical feasibility, we shall first review Proponents' Exhibit #8. Under the direction of Franklin T. Davis, CSMRI, a report titled "Capital and Operating Cost of a Suggested Process for the Removal of Fluoride Ion from Tailings Water" was prepared. The report shows applicability of currently available methods of fluoride removal and also details an as yet unproven method which has a potential of reducing fluoride content from 10 ppm to about 1 ppm at a rate of one million gallons per day.

The Davis report disposes of "state-of-the-art" systems as follows:



- A.  $\text{CaF}_2$  precipitation - economically unreasonable because of excessive calcium requirements.
- B. Contacting beds of activated alumina, calcium phosphate, calcium super phosphate or bauxite - prohibitively large bed volume required to treat large amounts of 10 ppm fluoride water, loss of bed material in regeneration and probable addition of phosphate ion to water.
- C. Combined magnesia-lime system - restricted to water containing less than 3 ppm fluoride, large amounts of magnesium co-precipitated.
- D. Carbon, zeolites and activated bone - best suited for low volume of water with a fluoride concentration of less than 5 ppm and a pH of 7 or less, regeneration losses.
- E. Ion exchange - low capacity, slow exchange, low fluoride selectivity and economics.
- F. Reverse osmosis and ion selective membrane - economically unattractive and not proven technology.

An alternate method proposed by Davis, but not yet tested, could be labeled as the "Hydroxyapatite Method". In that method water and lime are mixed to produce a 10% slurry which is reacted with 85% phosphoric acid to produce hydroxyapatite by the following reaction:



Twice the stoichiometric amount of hydrated lime is added to favor complete reaction of the phosphoric acid in the 1 hour reaction time.

Hydroxyapatite slurry is then pumped to an agitated reaction vessel where it contacts the incoming fluoride-bearing waste water. Reaction tank volume allows 1 hour for reaction of the fluoride to fluorapatite. From the reaction vessel the slurry flows to a flocculator tank where a flocculating polymer is added. After 15 minutes the treated slurry flows to a clarifier where suspended solids are settled. Overflow from the clarifier is discharged from the plant at a rate of 693 gpm. Sludge from the clarifier is pumped to the tailings dam but can be recirculated in varying amounts to the reaction tank in order to react any remaining unreacted hydroxyapatite. Sludge generation is small for this process and should not present any major disposal problem.

While Davis thinks the method looks good on paper, he quickly adds that additional laboratory studies are required to finalize a number of parameters before final evaluation is possible. Among the parameters to be determined are:

1. Ratio of lime to phosphoric acid and required reaction time,
2. Rate and absorption capacity of the hydroxyapatite, and
3. Optimum quantity of flocculant, flocculating time and settling time in the clarifier.

Capital investment for use of the hydroxyapatite method to treat one million gallons per day would be \$287,300, exclusive of roads, power lines and pipe lines. Operating costs for the plant were listed as \$11,278 per month or \$0.376 per 1,000 gallons.

Davis testified that Ozark-Mahoning would require three such plants since 3 million gallons of waste water must be treated (R. 172). Therefore, capital cost for Ozark-Mahoning would be in excess of \$1 million and operating costs would be \$45,000 per month (R. 171). Similar costs on a percentage basis would apply to Minerva's operations (R. 172).

Full-scale laboratory testing remains to be done for the hydroxyapatite method. Davis has performed some laboratory experiments using "artificial hydroxyapatite" with the result being a reduction to less than 1 ppm fluoride (R. 172).

As to other processes for removal of fluorides as described in Waste Water Treatment Technology, Second Edition, IIEQ Document 73-1 (Petitioner's Exhibit #9) Davis testified that none of the processes would be effective on mill tailings water. Davis stated that the processes would not be effective because most of the processes treat water that is relatively free of turbidity. Mill tailings water would have to be clarified or filtered in order to use the process and this "is expensive" (R. 168). Another reason for nonacceptance, according to Davis, was "although they don't say this, ...it is pretty obvious that after they removed it [fluoride] they dumped it back into the river downstream" (R. 167). This option is not open to Proponents.

After reviewing the various methods in the IIEQ document, the Board agrees that they do not directly relate to the fluorspar industry. However, a possible exception might be the use of contact beds of activated alumina. Without committing to the applicability of this process, the Board notes that one such unit in Bartlett, Texas has operated since 1952 on a municipal water plant to reduce fluoride from 8 mg/l to 1 mg/l. Noticeably absent from discussion on the Bartlett plant are flow rates and cost data. According to the report, two investigators experimented with an alumina bed as a polishing unit following lime precipitation. They found that a 30 mg/l residual fluoride concentration could be reduced to 2 mg/l. At a pH of 11.0 to 11.5 they were able to reduce fluoride from 9 mg/l to 1.3 mg/l. Regenerative losses were cited as 4% alumina lost per 100 regenerative cycles.

While such information is far too skimpy, it certainly raises the possibility of use on Proponent's mine waters, which are "reasonably clear" (R. 200), or on mill tailings water after clarification. Further, the Board finds nothing in the IIEQ document to indicate that any of the methods discussed involves subsequent dumping of removed contaminants "back into the river downstream".

In his letter dated April 26, 1974 (Petitioner's Exhibit #11), Davis said that new information supplied to Davis showed the mine waters to be free of turbidity. On this basis Davis states that the best process would be the one reported in "Defluoridation of Municipal Water Supplies", by F. J. Maier in the Journal of the American Water Works, August 1953. This is the same alumina contact bed process used in Bartlett, Texas and discussed just above. Davis states the process has a potential for lower capital cost than the hydroxyapatite method but laboratory verification would be required.

A set of figures based on the alumina bed process for mine waters and the hydroxyapatite method for tailings water, adjusted to 1974 prices, was supplied by Davis. These figures show a one million gpd tailings treatment plant with a fixed capital investment of \$298,000 and operating costs of \$12,800 per month. A 650,000 gpd mine water treatment plant to treat water from #7 Oxford Shaft, North Green Mine and West Green Mine and a 650,000 gpd mine water treatment plant to treat water from the Parkinson Mine and Barnett Air Shaft would require a fixed capital investment of \$568,800. Adjusted operating costs are shown as \$0.251 per 1000 gallons for the two mine water treatment plants and \$0.427 per 1000 gallons for the tailings plant for a total of \$0.328 per 1000 gallons. These costs exclude about 10,100 feet of right-of-way for pipeline which Davis warns may be "very substantial".

James N. Pappas, a Sanitarian with the U. S. EPA, attacked Davis' estimates of capital operating cost for the hydroxyapatite method. Pappas testified that these costs most likely would be considerably different if Proponents only treated the blow-down from a recycling process and where fluoride concentration was to be reduced to 2.5 mg/l rather than 1 mg/l. He stated that Proponents had not proved that recycling would be required and had failed to provide data relative to marketing of recovered fluorides as a possible cost reduction.

Davis responded (Petitioner's Exhibit #11) by stating that prior testimony had established "that recycling of tailings water in this type of flotation system is not compatible with the flotation system". He admitted that the water could be purified for recycling purposes but added that such a process would probably

be more expensive than the hydroxyapatite method because sodium ions and organics would have to be removed. C. B. Rash had testified that recycling adversely affected the efficiency of the flotation process (R. 41). Davis added that recycling efforts at the Colorado plant were not very successful. Solar evaporation ponds were required, which Davis adds, would not be practical in Illinois.

As to the possible sale of recovered fluoride, Davis responded that recovery of acid grade  $\text{CaF}_2$  from two million gallons of water would amount to about 240 pounds per day with a market value of about \$10.00. He added that he knows of no process from which  $\text{CaF}_2$  is recovered in a marketable form and that the whole idea is "a most impractical consideration".

In a letter dated May 16, 1974 Chris Potos, Chief of Water Quality Standards, U. S. EPA, suggested several possible methods of treatment which, in his opinion, raised doubts regarding the claim of economic hardship. Responding to the concern that during periods of low flow the water quality standard of 1.4 mg/l could be violated by an effluent which would be acceptable during periods of normal flow, Potos suggests that retention basins or lagoons could be utilized to store mine waters until sufficient flows upstream are available to allow release of mine waters without contravention of water quality standards. Potos hastens to add that the U. S. EPA does not necessarily recommend such a solution but merely raises the question "as to consideration of alternatives".

Other alternatives suggested by Potos included relocation of mills to sites near the Saline or Ohio Rivers and transmission of mill waste water from existing sites to the larger receiving streams.

Petitioner's Exhibit #11 was of particular concern to Potos. He questions whether generalized cost figures are applicable for specific projects. He states that treatment costs for reducing fluoride in mill tailings from 5 mg/l at the Minerva Mine #1 Mill to 2.5 mg/l at 580,000 gpd would probably be different than the cost of reducing fluoride in mill tailings from 10 mg/l to 2.5 mg/l at Ozark-Mahoning's Rosiclare Mill at 980,000 gpd. Further reduction of fluoride to 1 mg/l could amount to 90% of the total treatment cost according to Potos.

In his statement of treatment cost, Davis assumed that mine water flows from the Oxford, North Green and West Green Mines were 650,000 gpd. Potos states that Federal NPDES files show the flows to be only about 116,000 gpd. U. S. EPA files containing this information were not made a part of the record.

The Davis estimate also cited a 650,000 gpd flow to the "Barnett area waste treatment plant" from the Parkinson Mine and the Barnett air shaft. As Potos points out, Petitioner's Exhibit #13 shows flows from the Parkinson Mine, Barnett Mine and Barnett air shaft as 187,200 gpd.

If we were dealing with another type of industry it would be a simple matter at this point to combine the flows each proposed plant was to receive. These figures would show that the two proposed 650,000 gpd plants are substantially larger than required thus showing that the estimates of cost are overstated.

However, this industry must contend with substantial changes in mine discharges. In their Supplemental Submission Petitioners insist that a plant capacity of 650,000 gpd is necessary. Assuming for purposes of argument that it were both possible and practical to combine mine discharges from several mines at one (or more) location, Petitioner states that history would show the inability of the fluorspar industry, or anyone else for that matter, to anticipate increases in mine water as new veins are mined and new faces opened. For examples of the above, Petitioner cites the current discharge from Ozark-Mahoning W. L. Davis Mine which is now three times larger than the original discharge level. Minerva's older Gaskins Mine has a 1,260,000 gpd discharge as opposed to the 115,000 gpd discharge from the new Spivey Mine. Another example is the Crystal Mill facility which has a current discharge of 75,000 gpd during intermittent operations. If both the heavy media separation and flotation mill were placed into operation, this discharge would increase to as much as 480,000 gpd. Thus, Petitioners argue, it would be sheer folly to construct a treatment plant based on current operating requirements when these requirements might increase two, three, or more times in the months and years to come.

The basic premise necessary for such regional treatment plants is that the discharge flows from several points must be combined. Petitioner's concede that a project of this type might be accomplished if reasonableness and ability to finance the project were not to be considered.

Hurdles to be overcome by Petitioners in such a project are numerous and varied. Petitioners would have to commit finances covering the cost of land, easements, pipelines, electrical distribution lines, storage facilities, buildings, labor and maintenance for a theoretical process without any reasonable assurance that compliance would be achieved.

Pipelines and electrical distribution lines would have to cross land in the Shawnee National Forest. Petitioners state that past experiences considered, the U. S. Forest Service would be reluctant and probably unwilling to issue the permits necessary for such a project.

Petitioners also believe the concept of ponding or lagooning mine discharge is not a feasible alternative. Of the 15 discharge points from Petitioners mines and mills, one flows to the Ohio River and the remaining 14 flow to streams classified as intermittent streams. These discharge points are widely separated in the rock and hill terrain of Hardin and Pope Counties making centralization or combining of discharges impracticable. Numerous small treatment plants would have to be built. Petitioners state that 10 of the 15 discharges are currently in violation of the effluent or water quality standards.

As an example of the problems to be encountered if the ponding concept were implemented, Petitioners cite the following estimated cost for impoundment of discharge water from the Gaskins Mine for a 90 day period:

Total discharge for period = 113,400,000 gallons  
Estimated evaporation = 22,000,000 gallons  
Volume to be retained = 91,400,000 gallons  
Requires a 60 acre pond with average depth of 4.67 feet.  
Estimate need to purchase or lease 180 acres for pond site.  
Levee requires two feet of freeboard - 6.67 feet levee height.  
Requires moving approximately 31,000 cubic yards of dirt.

Cost:

Building levee at 60¢ per yard = \$ 18,400  
180 acres of land at \$300/acre = 54,000  
Cost of pipeline and pumps = 55,000  
Major expense total = \$127,000

In addition to the above estimated cost Petitioners would incur fees of \$200 per acre for land leased from the U. S. Forest Service (assuming such leases could be arranged) as well as cost for seed and fertilizer, pipeline right-of-way and maintenance.

However, Petitioner states that the major problem in ponding is that they are simply unaware of any land in the area suitable for ponds or lagoons.

One alternative available to Petitioner is to pump the discharge waters from Gaskin's Mine to the Ohio River, a distance of 7 miles. This project would require a 10" pipe, 40,000 feet long, costing \$320,000 according to Petitioner's estimates. Estimated total cost of this alternative including right-of-way, survey costs, legal fees, leases, piping, pumps and installation is in excess of \$420,000.

A second alternative would be to pump the Gaskin's Mine discharge to a central treatment plant serving all Minerva discharges. If this central plant were located at the Minerva Mill, the cost of pipe alone for the 15 mile project would be in excess of \$600,000 at \$8 per foot. Petitioners believe that a project of this magnitude would take longer than the remaining productive life of the Gaskin's Mine.

Responding to the suggestion that Petitioners consider relocation of mills near the Saline or Ohio Rivers, Petitioners state that they have no way of estimating the cost of such a project and that the project would be comparable in difficulty to relocating the Sears Tower.

The Board feels that Petitioners have shown that the many alternatives suggested are not practicable or economically feasible solutions to this complex problem. Hillsides blighted with pipelines and electrical power lines, especially in a national forest, makes these alternatives particularly displeasing from an aesthetic viewpoint in addition to the other drawbacks.

Olin's fluoride problem, as earlier noted, is substantially different from that of Ozark-Mahoning, Minerva or Allied Chemical. Nicholas J. Barone testified that Olin had investigated numerous fluoride removal techniques which were found to be unacceptable from an economic consideration. Olin's corporate engineering department devoted the efforts of some 50 people over a period of years on scaling up laboratory data to a full-scale operation intended for purchase and installation if the effluent standard was not changed.

Waste water from Olin's plant contains phosphate in proportions which enhance utilization of the lime process. Barone testified that the Olin fluoride removal process requires a ratio of phosphate to fluoride of 20 to 1 or greater or the process will fail to achieve the desired reduction (R. 232). An excess of lime of about 200% over stoichiometric is required to reach 2.5 mg/l fluoride.

The Olin process will require a capital investment of \$1.4 million and annual operating costs are estimated to be \$450,000 (R. 238). When operating, the Olin process will require 7 tons of lime and 28 tons of phosphate per day to treat the 1200 gpm waste water flow. About 70,000 lbs. of 35% solid sludge per day will be generated which will either be impounded or hauled to a landfill. Sludge disposal will cost an estimated \$80,000 to \$90,000 a year exclusive of land requirement cost (R. 240). Weighed against these factors will be the removal of an estimated 100 to 200 lbs. per day of fluoride (R. 288). Even with these process disadvantages, Olin believes it has a significant economic advantage over the other parties in this matter because of the phosphate

content of its waste water. The other parties would have to add phosphate to their waste water to make them treatable. Barone estimated that phosphate addition would increase operating cost by an additional 10 to 20% (R. 257).

The U. S. EPA's criteria for best practicable treatment of fertilizer industry effluent calls for achieving 15 ppm fluoride or a maximum of 30 mg/l fluoride for any 24 hour period (R. 243). The U. S. EPA's best available technology for the steel industry calls for reduction to levels of 4.2 to 8.3 mg/l fluoride on a 30-day average and 10 to 20 mg/l as maximum allowable for a 24-hour period (R. 246).

However, if the effluent standard were changed to Olin's proposed level of 10 mg/l, Olin could reach this level through "in-process controls" (i.e. pump leakage control, recycling, etc.). Fluoride in Olin's waste water comes in large part from leakage from over 800 pumps at the Blockson Works (R. 241). Barone testified that the reduction to 10 mg/l is a "very reliable number" (R. 269) based on actual experience at the plant (R. 254). Obviously the cost for in-process control would be far cheaper than installation and operation of a lime treatment process.

Allied Chemical's Metropolis plant effluent currently contains about 410 mg/l fluoride which is equivalent to a discharge of 7,000 lbs. per day fluoride (R. 375). Richard J. Sobel, Director of Environmental and Process Technology for Allied's Special Chemicals Division, testified that it is Allied's belief that technology is available to achieve 15 mg/l fluoride levels in the presence of calcium (R. 370). Allied is committed to a program aimed at an over-all level of 7 mg/l fluoride in the Metropolis plant effluent (R. 370).

Allied presented testimony in 1971 when the Board was considering the fluoride effluent standard. A. J. von Frank, Allied's Director of Air and Water Pollution Control, testified that it was a practical impossibility to achieve a fluoride level of less than 8.3 mg/l. This level represents the theoretical minimum that can be achieved in a water solution of calcium fluoride from the conventional lime method of fluoride removal (R. 371).

Sobel testified that Allied began a search of technical literature and an intensive in-house development program immediately after the Board adopted the 2.5 mg/l standard. This effort was directed toward discovery of a technically feasible and economically reasonable method of achieving the 2.5 mg/l standard. After two years of research and thousands of manhours, Allied concluded that there was no such method available.

Allied sought and was granted a variance from the fluoride effluent standard (and others) on February 28, 1974 upon satisfying



the Board that it was diligently working on fluoride abatement technology. Sobel testified that the abatement program approved in that variance will require about two years for completion at a cost in excess of \$4 million (R. 375). Research on fluoride removal technology will continue during the two year period.

Allied Chemical estimates that it would remove 6,880 lbs. per day of fluoride to achieve 7 mg/l. The capital investment for doing this would be \$2,683,200 and the operating costs would be \$660,000 per year. If the control equipment had a life expectancy of 10 years then capital costs would be approximately \$.107 per lb. of fluoride removed. Operating costs would be approximately \$0.26 per lb. of fluoride removed.

If Allied Chemical then used the most promising and technically feasible method to achieve 4.1 mg/l fluoride (filtration) an additional 33 lbs. of fluoride per day would be removed at a capital cost of \$220,110 (\$1.83 per lb. over a 10 year period) and an operating cost of \$73,000 per year (R. 377). If Allied then used a fixed alumina bed process to reach 2.5 mg/l, an additional 25 lbs. of fluoride per day would be removed at a capital cost of \$330,000 (\$3.62 per lb. over a 10 year period) and operating cost of \$99,000 per year (R. 378).

If the life expectancy of the abatement equipment is 10 years Allied Chemical would have capital costs of \$0.127 per lb. of fluoride removed. If the life expectancy of the equipment is 20 years then the capital costs for fluoride removal would be just \$0.064 per lb. The claim of Allied Chemical that capital costs would amount to \$9,480 per lb. per day is absurd. Allied's mistake was in failing to allocate the cost of the plant over the entire life expectancy. It seems obvious that the entire cost of the capital outlays should not be assigned to the first day of operation. The other companies which were participating in the hearings did not make this same mistake, but Allied Chemical made the mistake for them. (See Appendix A attached to Allied's final position paper). For instance, Allied claimed that capital costs for Ozark-Mahoning would amount to \$11,110 per pound of fluoride removed, apparently assigning a life expectancy of only one day for that proposed facility. Franklin Davis, the designer of the proposed Ozark-Mahoning system indicated that it would have a life expectancy of 20 years. Over a 20-year period the Ozark-Mahoning capital costs per pound of fluoride removed would be around \$1.50.

Allied Chemical did not tell us what the useful life of its control equipment will actually be. We doubt that the equipment installed at the Allied plant would have a life expectancy of 20 years. The U. S. EPA allows a depreciation factor of 10 years, and we have already noted that capital costs over a 10-year period would be less than \$.13 per pound of fluoride removed.

The Internal Revenue Code allows companies to take depreciation deductions for pollution control facilities over a five year period instead of the "estimated useful life" of the equipment. This practice inflates the cost figures attributable to the equipment during the period of depreciation, a fact Allied Chemical readily concedes. However, such costs could not under any acceptable accounting practice reach \$9,480 per pound.

Proponents mine water discharges do not appear in danger of violating the Mine Related effluent criteria of 8 mg/l. No testimony relating to the Mine Related Pollution Control Regulation was presented by proponents.

A remaining problem unique to Ozark-Mahoning and Minerva comes about as a result of mine discharges. Proponents contend that Rule 302(k) of the Water Pollution Control Regulations "proceeds to designate" as Secondary Contact and Indigenous Aquatic Life Waters "all waters in which, by reason of low flow or other conditions, a diversified aquatic biota cannot be satisfactorily maintained even in the absence of contaminants".

Rule 302(k) (As amended February 14, 1974) states:

"Secondary Contact and Indigenous Aquatic Life Waters"

Secondary contact and indigenous aquatic life waters are those waters which will be appropriate for all secondary contact uses and which will be capable of supporting an indigenous aquatic life limited only by the physical configuration of the body of water, characteristics and origin of the water, and the presence of contaminants in amounts that do not exceed the applicable standards.

The following are designated as secondary contact and indigenous aquatic life waters;

(k) All waters in which by reason of low flow or other conditions, a diversified aquatic biota cannot be satisfactorily maintained even in the absence of contaminants."

In its Opinion on this matter the Board stated:

"Part III contains water use designations. All waters are designated for general use except those in the restricted category, which has here been broadened in response to testimony to include waters whose flow is too low to support aquatic life. This should relieve the burden of treatment beyond the effluent standards

for discharges to intermittent streams. Such extra effort is difficult to justify when it will not result in a satisfactory aquatic life because of insufficient flow." (Vol. 3, p. 765).

The request of the mining companies that certain waters be designated "Secondary Contact and Indigenous Aquatic Life Waters" is important, because such designation would substantially increase the allowable fluoride levels in the stream.

Rule 402 of the Water Pollution Regulations provides:

"In addition to the other requirements of this Part, no effluent shall, alone or in combination with other sources, cause a violation of any applicable water quality standard. When the Agency finds that a discharge that would comply with effluent standards contained in this Chapter would cause or is causing a violation of water quality standards, the Agency shall take appropriate action under Section 31 or Section 39 of the Act to require the discharge to meet whatever effluent limits are necessary to ensure compliance with the water quality standards. When such a violation is caused by the cumulative effect of more than one source, several sources may be joined in an enforcement or variance proceeding, and measures for necessary effluent reductions will be determined on the basis of technical feasibility, economic reasonableness, and fairness to all discharges."

Therefore, if we adopt an effluent standard of 15 mg/l, the discharges must meet that effluent standard and also must not cause a violation of the Water Quality Standard beyond the mixing zone. The mining companies could meet a Water Quality Standard of 5 mg/l fluoride.

If on the other hand, the water quality standards were held at the present 1.4 mg/l criteria while the effluent standard is changed to 15 mg/l, the mining companies would still have a problem during periods of low flow when effluent from the mines is proportionately a larger part of the stream. Several alternatives would have to be considered by the mining companies:

1. The mining companies could petition to have the stream declared a "Secondary Contact and Indigenous Aquatic Life Water" under Rule 302(k). Water so designated would have a water quality standard identical to the new 15 mg/l effluent standard (See Rule 205).
2. Ponding--This concept has already been discussed and found to be impracticable for the mining companies.

3. Treat the effluent down to the water quality standard of 1.4 mg/l. This alternative would cause undue hardship on the mining companies.

4. Variance--This is available only on a temporary basis while permanent solutions to the problem are brought into play.

The record for reclassification of the streams is woefully inadequate. While numerous streams are known to be receivers of the mine water discharges, proponents sole presentation on the issue is a copy of an Agency report on biological samples taken on Big Grand Pierre Creek. As earlier noted, results of this survey indicate well-balanced benthic invertebrate populations both upstream and downstream from the mine discharge. One stream was found to be "semi-polluted".

If the Board were to act at this time on the information presented, the obvious decision would be to deny the "secondary contact" classification. However, the Board feels that no decision is required at this time on the Rule 302(k) matter simply because Rule 302(k) was not adequately addressed as an issue during these proceedings. Our ruling does not preclude Proponents from raising the Rule 302(k) issue at some later date. Our decision only relates to the inadequacy of the record now before the Board on that matter.

It is the Board's finding that Proponents, with the aid of Olin and Allied, have presented proof sufficient to warrant changing the fluoride effluent limit from 2.5 mg/l to 15 mg/l. Effluent of that quality should be acceptable in Illinois waters. The Water Quality Standard for fluoride remains unchanged at 1.4 mg/l for all dischargers other than the fluorspar mining and concentrating industry. The Water Quality Standard becomes 5 mg/l fluoride in waters which receive effluent from the mines and mills of the fluorspar mining and concentrating industry, and have been designated by the Illinois State Water Survey as streams which once in 10 years have an average minimum seven day low flow of zero.

Throughout these proceedings some degree of importance was attached to information in the Illinois EPA's Public Water Supplies Data Book, July 1973. In that document, fluoride levels in drinking water as high as 7.7 mg/l fluoride for Bureau Junction and 5.8 mg/l for Parkersberg are shown. Proponents state that they are not aware of any Agency initiated proceedings, enforcement or otherwise, because of the fluoride level in these public water supplies. However no evidence was introduced regarding the impact of these fluoride levels in these communities, and we certainly do not infer from the lack of legal action that 5.8 mg/l - 6.6 mg/l is an appropriate standard for the entire state.

It is the responsibility of this Board, as charged by the Environmental Protection Act, to protect the quality of the environment. Having reviewed all aspects of these proceedings, the Board feels that an increase in the general water quality standard for streams receiving fluoride containing discharges from the fluorspar mining and concentrating industry, without change for other streams in the State, would not create significant and unwarranted effects on the environment. Unrefuted testimony and evidence in the record shows that no apparent environmental damage has occurred in these streams because of continuous mine discharges over a number of years.

In raising the water quality standard and the effluent limitation for fluoride, the Board has carefully taken into consideration the expected impact upon the receiving streams and the economic impact of the Regulation. Ozark-Mahoning and Minerva will receive relief for operation of their mines and concentrating mills. Ozark-Mahoning's current discharge level of 10 mg/l is below the new effluent limit and should not require any additional treatment barring a major process upset. Minerva, on the other hand, discharges water from its Mill #1 and Crystal Mill that are well within the 15 mg/l limit. Thus, Minerva will not be required to provide any additional fluoride control treatment unless process changes cause the fluoride concentration to increase significantly above the current concentrations.

In those instances where Proponent's mines discharge to flowing streams, current effluent levels appear to be low enough to preclude violation of the 15 mg/l effluent criteria. A different situation confronts Proponents when and if their mine discharges go to dry or intermittent streams. For the most part, mine discharges are well below the new 5 mg/l water quality standard for such streams. Pond #3 of Minerva's Mine #1 and Mill now average 4.5 mg/l and Minerva will have to monitor this discharge closely to insure that this discharge does not violate the new standard. With proper chemical treatment Minerva should be able to maintain this discharge concentration within the new limits.

Increasing the effluent limit to 15 mg/l will provide significant relief for Olin since that level can be reached by implementing "in process controls". In process controls, according to Barone's testimony, will involve some repiping, recycling of certain waste streams, elimination of chronic leaks and possibly some equipment modifications or replacement. Barone testified that Olin considered in process controls to be "a very attractive thing" since the operating costs would be so low as to not even show up as a separate cost (R. 242).

Through the recycling effort Olin would actually receive some benefit since phosphate materials now being discharged would be recovered and end up as product instead of waste. Olin did not

have any cost figures relating to in process control but Barone testified that the capital investment would be "much lower" than installing a lime treatment plant (R. 242).

This change in effluent criteria for fluoride affects Allied differently since the current fluoride concentration in Allied's effluent is significantly higher than that of any other party in this matter.

At one time in these proceedings Allied sought to change the effluent standard to allow 15 mg/l fluoride based on the average of 24 hour composite analysis for thirty consecutive days and 30 mg/l maximum for any one 24 hour composite. In its last submission Allied states that its recommended standard of 30 mg/l for any one 24 hour composite may prove to be too restrictive for some industries such as hydrofluoric acid manufacturers. Allied now seeks to change the effluent limit to 30 mg/l as the average of 24 hour composites for 30 consecutive days and 60 mg/l for any one 24 hour period.

Allied's original recommendation was based upon criteria published in Volume 39, No. 49 of the Federal Register on March 12, 1974 by the U. S. Environmental Protection Agency. The reasonableness of this U. S. EPA criteria was challenged by the hydrofluoric acid manufacturers in the Fourth Circuit Court of Appeal. One result of this action, according to Allied, is that the U. S. EPA now plans to revise the fluoride effluent limitations to the same limits Allied now seeks in this matter. Although the U. S. EPA has not yet proposed any new limits, Allied states that Region VI of the U. S. EPA granted Allied a permit for its Baton Rouge Works on December 9, 1974 using the new limit.

Allied is now committed to a fluoride reduction program designed to achieve a fluoride concentration in its effluent of 7 mg/l. Undoubtedly, Allied will modify this program to meet the fluoride level now permitted and we would expect this modification to reduce cost.

Having considered all information in this record concerning the technical feasibility and economic reasonableness of alternative methods of fluoride abatement in conjunction with the data from a commercial lime treatment facility now in operation at another Allied facility it is our finding that the 15 mg/l fluoride is both economically reasonable and technically feasible when applied to Allied Chemical.

ORDER

It is the Order of the Pollution Control Board that the Water Quality Standards and the Effluent Standards of the Illinois Water Pollution Control Regulations be amended to specify the following limitations for fluoride:

PART II WATER QUALITY STANDARDS

203.1 Exceptions to Rule 203

(a) The fluoride standard of Rule 203(f) shall not apply to waters of the State which:

- (1) receive effluent from the mines and mills of the fluorspar mining and concentrating industry, and
- (2) have been designated by the Illinois State Water Survey as streams which once in ten years have an average minimum seven day low flow of zero.

Such waters shall meet the following standard with regard to fluoride:

<u>Constituent</u>	<u>Storet Number</u>	<u>Concentration (mg/l)</u>
Fluoride	00950	5

PART IV EFFLUENT STANDARDS

408 - Additional Contaminants

(a) The following levels of contaminants shall not be exceeded by any effluent:

<u>Constituent</u>	<u>Storet Number</u>	<u>Concentration (mg/l)</u>
Fluoride (total)	00951	15

I, Christan L. Moffett, Clerk of the Illinois Pollution Control Board, hereby certify the above Opinion and Order was adopted this 6<sup>th</sup> day of March, 1975 by a vote of 4 to 0.

