ILLINOIS POLLUTION CONTROL BOARD September 7, 1978

IN THE MATTER OF:

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R74-15, -16

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WATER POLLUTION CONTROL AMENDMENTS: CYANIDE

OPINION OF THE BOARD (by Mr. Goodman):*

The original Petitions for a Regulatory Amendment in this matter were filed approximately four years ago by Republic Steel Corporation and the Illinois Petroleum Council (R74-15 and R74-16, respectively). The Petitions sought changes in the Board's Water Quality, Effluent and Sewer Discharge Standards for cyanide.

BACKGROUND AND PROCEDURES

This Board inherited the substance of its cyanide regulations from its predecessor in water pollution control, the Illinois Sanitary Water Board. The Sanitary Water Board's cyanide water quality and effluent standards were contained in various individual regulations, applying to various river basins and dischargers, as well as in rules of general applicability. <u>See</u>, <u>e.g.</u>, SWB 5; SWB 10, at Rule 1.04(d)(1966); T.R. 20-19, Rule 1.01 (1964); SWB T.R. 20-22, at 2 (1968). The last of those references limited effluents, discharged to waters of the state, to cyanide concentrations of 0.025 mg/l, with the footnote, "reduced [sic**] at least to cyanate and approaching zero as CN."

In 1972, as part of its codification and general review/ revision of existing Water Pollution Regulations, this Board adopted the same general standard of 0.025 mg/l for water quality

^{*} The Board wishes to thank Vincent P. Flood, Jr., Attorney, and Carolyn Hesse, Technical Assistant to the Board for their assistance in the preparation and drafting of this Opinion and Order.

^{** &}quot;Reduced" is probably used colloquially, and not to indicate a chemical reaction.

and effluent use, but revised the old SWB standards for sewer dischargers. In making that decision, the Board cited as its justification the work of the Ohio River Sanitary Commission (ORSANCO), carried on in the late 1950's and early 1960's, (See, eg. Ex. 10, 11, 12).

ORSANCO's uncertainty in two areas -- distinction between various cyanide forms and the availability of adequate measurement techniques -- therefore led to the Board's adoption of the general 0.025 mg/l standard. An attempt by industry and others to resolve those uncertainties, along with other technical and economic factors, forms the basis for the regulatory proposals now before the Board. The proponents, along with various other participants in this proceeding, contend that the 0.025 mg/l standard can and should be changed for the following reasons:

1. The existing effluent, water quality and sewer discharge standards for cyanide fail to distinguish between various cyanide chemical forms which are significantly different in terms of toxicity and treatability; and

2. Any need for those standards which may have existed as a result of testing procedure inadequacy or other uncertainty no longer exists, since technology has advanced to the degree necessary for such measurement determinations (although complete accuracy was not alleged at any point).

At hearing, evidence was also presented to support the following additional contentions:

3. In many cases, individual industries or dischargers cannot, using practical technology, comply with the existing 0.025 mg/l effluent standard for "total" (a term defined below) cyanide.

4. Even in those cases in which the removal of cyanide to meet the 0.025 mg/l standard is technically practicable, it is for many industries economically unreasonable to require such treatment.

5. Since cyanide is more readily and economically treated in municipal treatment works, it is unreasonable to severely limit discharges of cyanide into

sewers tributary to such municipal treatment plants, (in accord with the existing sewer discharge criteria of Rule 703) whether or not a municipal discharger can presently meet the existing 0.025 mg/l standard.

In addition to the general relief asked in the original Petitions, various other proposals and amendments were offered during the hearings in this matter. For example, the Metropolitan Sanitary District of Greater Chicago (MSDGC) requested special relief for the secondary contact and indigenous aquatic life waters to which certain of its treatment plants presently discharge. (It was the MSDGC's contention that the existing, or even the proposed, levels of protection are not necessary for those waters.) In a separate proposal, the Illinois Environmental Protection Agency (IEPA) made particularly specific proposals on the issue of testing and measurement for various cyanide chemical forms and quantities.

Fifteen hearings on the various proposals and submissions were held in Chicago and Springfield from June 16, 1975 until May 17, 1977. The IIEQ filed its study, IIEQ Doc. No. 77/3, "Economic Impact of Alternative Cyanide Standards in Illinois", on February 25, 1977. In addition, various participants introduced extensive economic data throughout the "merit" hearings. At the conclusion of the hearings on this matter, the record consisted of thousands of pages of testimony and documentary exhibits. Republic Steel Corporation and the Illinois Environmental Protection Agency (IEPA) also filed thorough, extensive briefs summarizing that evidence.

In addition to the Regulatory Proposals filed by Republic Steel and the Illinois Petroleum Council, various other participants also filed, presented in testimony or supported various other recommended standards for cyanide. Those recommendations or proposals are summarized on the following page, (Table taken from Appendix 4, Brief of Republic Steel Corporation).

DISCUSSION

Chemical forms of cyanide

Much of the testimony in the record centered on the differences in toxicity, treatability and formation of various cyanide containing molecules. The principle forms of cyanide discussed follow:

1. Free cyanide includes the triple bonded carbonnitrogen anion (C \equiv N⁻) and hydrogen cyanide (HCN), also

(CYANIDE CONCENTRATIONS IN MILLIGRAMS PER LITER)

	WATER QUALITY (Rule 203(f))	EFFLUENT (Rule 408(a))	SEWER DISCHARGE (Rule 703(a) and (b))
PRESENT REGULATIONS	0.025 total	0.025 total ¹	0.025 total (Rule $703(a)$) ² 10 total/2 readily releasable (Rule $703(b)$) ³
REPUBLIC STEEL	1.0 total/0.025 free	2.0 total/0.1 free	2.0 total/0.1 free (Rule 703(a) ² 10 total/2 readily releasable (Rule 703(b)) ⁴ 10 total/2 readily releasable (Rule 703(b)) ³
ILLINOIS PETROLEUM COUNCIL	0.025 free	0.1 free	10 total/2 readily releasable ⁴
METROPOLITAN SANITARY DISTRICT	0.1 total ⁵	0.1 total ⁶ 0.3 total ⁷	
ILLINOIS EPA	0.025 total ⁸	0.1 total ⁹	0.1 total (Rule 703(a)) ² 10 total/2 readily releasable (Rule 703(b)) ³
ILLINOIS IIEQ		0.1 total ¹⁰	
U.S. EPA	0.025 total ¹¹		
DUPONT	0.025 free	12	

¹According to Rule 401(c), compliance with the effluent standard shall be determined on the basis of 24-hour composite samples (i.e., daily average). In addition, for any given grab sample (daily maximum), the total cyanide concentration shall not exceed 0.125 total (five times the numerical standard).

²No permit required, but violation must not occur "at any time". This provision governs sewer discharges which are not subsequently treated.

3 With permit only if no violation of the effluent standard by the downstream sewage treatment plant occurs.

⁴Without permit if no violation of the effluent standard by the downstream sewage treatment plant occurs.

⁵For secondary contact and indigenous aquatic life waters (include the Calumet River). The MSD's original proposed water quality standard of 0.025 "simple" was withdrawn in April, 1976.

⁶For sewage treatment works other than the Calumet River STW. The MSD's original proposed effluent standard of 1.0 total/0.1 "simple" was withdrawn in April, 1976.

⁷For the Calumet STW only.

⁸As part of the IEPA's proposed water quality standard, the coefficient of variation (which is a measure of the single operator-single laboratory precision) shall not exceed 20% at the 0.025 mg/l level and the bias shall not exceed 10% of this level.

⁹The IEPA effluent standard proposal provides that compliance measurement shall be with such precision that the coefficient of variation does not exceed 10% and the bias does not exceed 20%.

¹⁰Compliance is to be determined by 24-hour composite samples averaged over 30 days. No single 24-hour composite sample shall exceed 0.2 total (Twice the numerical standard), and no single grab sample shall exceed 0.5 total (5 times the numerical standard).

11Compliance is to be determined by 24-hour samples. No single grab sample shall exceed 0.050 total (twice the numerical standard). The IIEQ proposal also provides for site-specific effluent standards in certain cases where a less stringent effluent standard would be appropriate.

-²Effluent limitations to be established on a case-by-case basis to insure that the water quality standard within reasonable mixing zone, is not exceeded.

referred to as hydrocyanic acid when dissolved in water. These two forms of cyanide exist in equilibrium in aqueous solutions. HCN is the predominant form in neutral and acidic solutions; at higher pH's hydrogen cyanide dissociates to form cyanide ion.

2. <u>Simple cyanides</u> are compounds that contain a positive ion (cation) and x number of cyanide ions where x is equal to the valence state of the cation. The cation could be an ammonium group, alkali (metal), alkaline earth or heavy metal. Generally, the cyanide compounds can dissociate in water to release the cation and the cyanide ion(s). The range of solubility and dissociation depends on the molecular structure of the given compound.

3. <u>Complex cyanides</u> are compounds in which one or more cyanide ions are joined with a metal atom to form a complex negative ion, which may in turn join with a positive ion to form a molecule. Complex cyanide can be represented as $A_{y}[M(CN)_{x}]_{z}$ where A represents the cation, CN is the cyanide group, $M(CN)_{x}$ is the metal-cyanide complex ion, and x, y, and z represent the numbers of ions in the molecule. When dissolved in water, complex cyanide molecules may dissociate to release the complex ion, $M(CN)_{x}$ and the positive ion. The metal-cyanide complex ion may further dissociate to release the cyanide ion. The rate and degree of dissociation under various conditions, such as temperature and pH, depends on the cyanide complex; some complexes readily dissociate while others are stable.

4. <u>Readily releasable cyanides</u> are not subject to accurate chemical definition and are defined strictly by regulation. In the existing Rule 703(b), readily releasable cyanides would include any free, simple, and complex cyanide compounds in a sample which release free cyanide when subjected to a temperature of 150°F. at a pH of 4.5 for thirty minutes.

5. <u>Total cyanide</u> is simply the sum of all of the above cyanide forms, along with any other compounds or cyanide forms which, depending on the testing method used, are recorded as cyanide. Throughout the hearings in this matter, total cyanide was used to denote any and all cyanide, in any form, present at any time. 6. Other cyanide forms, e.g., organic cyanides such as cyanohydrins, are important only insofar as they fall into one of the above categories or act as interferences in various analytic or treatment methods.

Toxicity

Although some complex cyanides have been shown to be toxic to aquatic life, (R.1364-1365) it is generally agreed that hydrocyanic acid (HCN) is the most toxic form of cyanide. There is some information which indicates that the toxicity of complex cyanides is related to their dissociation to form free cyanides which in turn depend on water conditions such as pH, turbidity, and temperature (R.1540). Cyanide intoxication results in cellular asphyxia and leads to death (R.990).

Several witnesses presented testimony on cyanide toxicity for aquatic life; four of them, Pipes, Doudoroff, Broderius, and Lue-Hing had actually performed cyanide toxicity testing on various organisms. It appears that fish are the most important organism that would be affected by cyanide in the concentrations discussed in this proceeding. Generally, cold water fish, such as trout and salmon, are more sensitive to cyanide than are warm water fish, such as fathead minnows, bluegills, and bullheads. Pipes found a four day LC50* of 0.05 to 0.1 milligrams HCN per liter for trout and salmon and an LC50 of 0.16 to 0.24 mg/l for warm water fish (bluegill, sunfish, fatheat minnows) (R.95). Doudoroff reported toxicity tests using bluegills which showed 48 hour LC₅₀ values for free cyanide of 0.15 mg/l, for cuprocyanide ion (complex copper cyanide) of 4 mg/l and for nickel cyanide complex and iron cyanide complex on the order of 400 Lue-Hing, of the Metropolitan Sanitary District of mq/1. Greater Chicago, exposed fathead minnows to unchlorinated sewage treatment plant effluents for 96 hours and reportedly did not obtain fish kills (R.1118-1119). However, it should be noted that the cyanide concentrations used in the MSDGC test were less than the reported 96 hour LC_{50} of 0.18-0.23 mg/l as free cyanide for fathead minnows and less than the standard set forth in this Opinion.

Broderius has done and, at the time of the hearings, was still doing an extensive amount of research on cyanide. Table 1 of his testimony (R.854) is based on the work of others and presents minimum lethal threshold concentrations of free cyanide

^{*} A four day LC₅₀ is the lethal concentration that would kill half of the test organisms within four days (96 hours).

for various species of fish. Based on his own work using continuous flow bioassays, Broderius has found minimum lethal threshold concentrations to be generally less than the concentrations reported in Table 1 (R.851). The differences in data are probably due to significant changes in the cyanide level in the water produced by the metabolism and absorption of cyanide by fish and by loss of cyanide (HCN) to the atmosphere (R.853). Hence, data from static bioassays would tend to indicate that fish could tolerate a higher concentration of cyanide than would data from the more accurate continuous flow tests in which the cyanide concentration is kept constant. Broderius concluded that free cyanide concentrations near 0.1 mg/l as CN have eventually proven fatal to a high percentage of cold and warm water fishes and that levels greater than 0.2 mg/l are most likely rapidly fatal for most fish species (R.855).

Exposure to free cyanide at levels less than minimum lethal threshold concentrations has been shown to produce sub-lethal effects. Broderius reported finding biochemical changes, avoid-ance reactions, reduction in swimming performance, and reduced fertility and fecundity at levels of HCN as low as 0.012 mg/l in the laboratory (R.863-869). Pipes also testified that fish avoid toxic concentrations of free cyanide (R.104).

Human toxicity was discussed by two witnesses, Hermann and Carnow. Hermann noted that the "minimum oral dose of <u>free</u> cyanide which may produce a fatality in adult humans has been reported to range from 20 mg to 100 mg," (R.82) which is far in excess of any of the standards being set forth in this matter. Although he did not have data to substantiate his claim, Carnow argued that there may be human chronic toxicity effects from exposure to sub-lethal concentrations of cyanide (R.2015-2076). However, it seems unlikely that these effects would occur at the low concentrations set forth as standards in this proceeding.

Hermann also testified that the sewer discharge limitations would protect sewer workers under the worst conditions that would be expected in a sewer. According to his calculations, if the wastewater has a pH of 4.5 and a temperature of 150°F (65.5°C) and the sewer is completely unventilated, HCN in the sewer air could not exceed 10 ppm (the threshold limit value set by American Conference of Governmental Industrial Hygenists) unless the wastewater contained free cyanides in excess of 3.8 mg/l for an extended period of time (R.85). The cyanide sewer discharge standard of 2 mg/l readily releasible and 10 mg/l total should provide an adequate margin of safety.

Measurement Techniques

There was much testimony presented in the record on the various measurement techniques for cyanide. The following is a brief summary of the material in the record; for more detail, see the testimonies of the following witnesses: Caruso, Doudoroff, Lee, Hernandez, Mathre, Lue-Hing, Broderius, and Schaeffer.

Measurement techniques for total cyanide involve liberating cyanide from the sample as HCN then collecting and analyzing this cyanide by using various procedures. The three methods approved by the USEPA for measurement of total cyanide are: (1) ASTM D2035-A: Total Cyanide, 1972; (2) Standard Methods for the Examination of Water and Wastewater, 13th Edition, 1971 - Total Cyanide; and (3) USEPA Method - STORET No. 00720, 1971 - Total Cyanide (R.662). Reportedly, the tests have a precision (reproducibility) of plus or minus 80 to 100 percent at a total cyanide concentration of 0.025 mg/l (R.663). Hernandez evaluated the methods for measuring total cyanides (Exhibit No. 31) and concluded that the USEPA method is the best available method for measuring total cyanide since thiocyanate can reportedly interfere with the ASTM-A method and the Standard Methods measurement technique does not achieve recoveries of total cyanide as high as the recoveries reported for the USEPA method (20 to 80 percent recovery for Standard Methods versus 90 percent for the USEPA method).

Although some of the proposed standards would set limits on free cyanide, there is no generally accepted method of analyzing a water sample for free cyanide (R.65, R.1712, R.1441). However, four methods of approximating the concentration of free cyanides were identified (R.669-670). They are: (1) ASTM D2036-B: Cyanides Amenable to Chlorination; (2) Technicon Automated Method; (3) AISI-Modification of ASTM D2036-A; and (4) Wood River Modification of the Roberts-Jackson Method. These methods also involve liberating cyanide from the solution as HCN and then collecting and analyzing it. The major difference between the methods for measuring total cyanide and the methods for estimating free cyanide is that the distillation step in the former is more severe in order to break down the complexed cyanide. Even though these methods are said to be conservative because they measure some complex cyanides as well as free cyanides, the particular complexes included and the extent to which they are included is unknown. An additional problem with these four methods is that, according to IEPA testimony, the technique for preserving the

samples destroys free cyanide and disturbs the equilibrium which causes the complex cyanide to convert from one form to another (R.1441). In addition, some of these test methods are plagued by interference or poor sensitivity (R.670-672, R.1382-1384, R.1427). It appears that none of these procedures is generally applicable to samples of all wastes. Hence, the IEPA does not support any method which supposedly measures "free" cyanide (R.1392).

Sources

Although cyanide is a naturally occurring compound and may at times reach levels in water which are toxic to aquatic life as a result of natural processes, such occurrences are unlikely in Illinois. Despite some anamolies in Metropolitan Sanitary District figures, indicating unusually high cyanide levels from non-industrial areas, the bulk of cyanides present - whether free or complex - in Illinois waters result from industrial processes associated with the metal plating industry, the manufacture of iron and steel, or petroleum refining.

Of the various industries discussed at these hearings, with the minor exception of steel case hardening operations, only the metal plating industry purposely uses cyanide in high concentrations. Cyanide-containing plating vats are still used in most plating shops, although other technologies have been investigated. (In many cases, no substitute for cyanide has been found.) Cyanide bearing wastes originate in the vats themselves, subsequent rinses, drippings and spills. Although cyanide wastes from the plating industry typically contain high concentrations, they are relatively low in volume.

Cyanide is generated in the iron and steel industry in four operations (of which the first three are significant in terms of quantity of cyanide produced):

1. Large volumes of typically low (1 mg/1) concentrations of cyanide wastes are generated in the scrubbing steps for blast furnace gases.

2. Blast furnace gas cooling water also contains large quantities of wastes with a relatively low (2 mg/l) concentration of cyanide. The source of the cyanide in these wastes is the same as that in blast furnace gas scrubber water, above. 3. By-product coke operations produce, in the cooling process, relatively high (e.g., 90-100 mg/1) concentration cyanide wastes, typically composed of a mixture of simple, free, and complex (including iron) cyanides.

4. Steel case hardening often involves the use of sodium cyanide vats; cyanide bearing waste waters are generated in subsequent rinses.

In the petroleum refining industry, cyanides are generally formed in the cracking and coking operations. The amount of cyanide produced varies greatly, apparently dependent on the amount of nitrogen present in the crude oil being refined. Oil refinery cyanide wastes are often complex cyanides and include ferricyanide and/or ferrocyanide.

In addition to the above sources of cyanide, other unknown sources contribute to cyanide discharges from municipal treatment plants, (e.g., R.1113). Even completely domestic, "bedroom type" communities without a significant industrial waste load may, at times, exceed the current 0.025 mg/l limitation for cyanide (R.1148).

Fates of Cyanide in the Environment

Free and complex cyanides are subject to alteration from their original state upon introduction to the aquatic environment. Free and simple cyanides may be oxidized biologically, escape to the atmosphere, or combine with other substances to form complex cyanides; cyanides already in complex form may, on the other hand, dissociate to form toxic free cyanides. The reactions involved are all reversible, accelerable, and interactive.

The importance of these reactions is that they are central to the primary contention of the proponents and several other participants: that complex cyanides, if allowed to enter the environment in increased quantities, will not cause environmental damage. The Board, therefore, must determine whether complex cyanides, especially iron cyanides, will be converted in the environment to toxic free cyanide in quantities sufficient to cause problems. The Petitioners argued at length, and presented testimony and evidence accordingly, that many complex cyanides -in particular, iron cyanides -- dissociate very slowly, if at all, in the environment. Although there are many forms of complex cyanide, discussion at hearing and in the exhibits entered in this matter centered upon iron cyanides since, as mentioned above, alkaline chlorination does not destroy iron cyanides and the iron cyanides appear to be one of the less toxic forms. The principal forms under discussion were ferrocyanide (hexacyanoferrate (II)) and ferricyanide (hexacyanoferrate (III)). Although the former may be transformed to the latter and other, minor differences may exist, the two forms may be treated as a single form for regulatory purposes.

-Much discussion revolved around the photodissociation of iron cyanides to free cyanide. (See testimonies of Broderius, Caruso, and Lue-Hing.) In short, it is clear that laboratory conditions, with distilled water and iron complex cyanides, will give photodissociation results quite possibly toxic to aquatic life, starting with iron cyanide complex concentrations of less than 1.0 mg/l and possibly down to 0.1 mg/l. However, it is difficult to extrapolate these findings to the natural environment.

Only one study has been done to date using natural waters and existing discharges and was performed by MSDGC. Dr. Lue-Hing contended that MSDGC's measurements in the Illinois River, when compared with upstream discharge and water quality data, indicate slow and insignificant photodissociation. (The MSDGC found an average of 17%, with a range of 4 to 30%, "simple" cyanides downstream in the Illinois River.) (Exhibit #51). That conclusion was, however, strongly rebutted by IEPA since the Illinois River is not necessarily representative of all the waters of the state. It should also be borne in mind that the river was only sampled on one occasion.

It appears that the photodissociation of iron cyanide complexes may indeed cause the release of significant amounts of toxic, free cyanides under some circumstances. The reaction involved, however, is inhibited or accelerated by many factors, including pH, temperature, sunlight, and the presence of other compounds.

Treatment Technology

There was general concurrence among all witnesses discussing the subject that no generally applicable treatment process is capable of consistently producing an effluent meeting the existing 0.025 mg/l standard. In addition, it was also agreed that it is not possible to eliminate cyanide use or formation from most of the industrial processes discussed above. The various available treatment methods are, therefore, discussed briefly.

Seemingly contrary to the general consensus just described, complete cyanide destruction has been achieved by at least one method currently in use in Illinois. Incineration is presently being employed by one refinery, which has a nearby heat source available. This is not, however, a generally applicable technology. Few dischargers have available the necessary surplus heat source(s), and few (if any) of those who do also have a high-concentration, low-volume waste stream such as that currently being incinerated. Steel industy wastewater streams in Illinois, for example, generally exceed 10,000 gallons per minute, and some may exceed that figure by orders of magnitude.

Alkaline chlorination, on the other hand, is the most commonly used method for the treatment of cyanide-bearing wastewater. It involves the addition of chlorine to highly alkaline (pH of 10 or greater) wastewaters to oxidize the cyanide present. While free cyanide concentrations of 0.1 mg/l or less can be obtained by alkaline chlorination, it is not generally considered effective for the control of iron cyanides. (See generally, testimony of Dr. Patterson and Exhibit 49).

Other treatment methods are rarely used. In general, they are either experimental, inadequate to achieve sub-milligram per liter effluents, or are considered too costly for reasonable use. They are:

(1) Alkaline ozonation is merely the use of ozone instead of chlorine to oxidize cyanides. This method has difficulties resulting from the inability to oxidize certain complex cyanides, high capital and operating costs, and sludge production.

(2) Oxidation with permanganate, still in the laboratory development stage, will not destroy several important complex cyanides. It also suffers from high cost and sludge production.

(3) Electrolysis is capable of destroying almost all cyanide species, including complex iron cyanides. However, costs would obviously be quite high for any except high-concentration, low-volume waste streams, as with incineration, (e.g., R.150 et seq.; Ex. 16). It was only suggested for metal plating wastes. (4) Precipitation does not destroy cyanides, instead it merely concentrates them for disposal by other means. In addition to a very large sludge accumulation, this method is not practical because it has not been shown to achieve effluent cyanide concentrations below 4 or 5 mg/l.

(5) Ion exchange would be applicable only to low-volume waste streams. In addition, the method is impractical due to interferences, which include almost any other _______impurity in the water being treated.

(6) Adsorption with catalytic oxidation requires the addition of copper in large quantities, probably with resulting violations of copper effluent standards. In addition, the method is not applicable to steel industry or oil industry wastes as a result of interferences.

(7) Conventional biological treatment has removed approximately 55% of influent cyanide at MSDGC's Calumet STP. However, excessive influent loading can impair the biological removal mechanism and interfere with plant operations, and shock loadings are a serious problem (as described by the Rockford Sanitary District). Some of the cyanide removal may be due simply to concentration in sludge. This method is not generally effective for some strongly complexed cyanides.

(8) Other methods are detailed in Ex. 16 and elsewhere in the record, including IIEQ Doc. No. 76/22. These include such exotic techniques as gamma ray irradiation and are not beyond laboratory testing; most would, even if proven successful, be applicable only to very lowvolume waste streams.

In summary, it is clear that -- except in very-high-concentration situations such as might exist in the metal plating industry -alkaline chlorination is the only practical treatment method and destroys approximately 80% of all cyanides amenable to chlorination (R.760). While it has problems, including particularly interferences in oil and steel industry wastes, it is the only method reasonably available for high-volume wastes. Dr. Patterson's testimony indicated that alkaline chlorination may be considered available, practical treatment technology, capable of allowing most dischargers to meet his recommended standard of 0.1 mg/l total cyanide.* Steel industry witnesses, including Drs. Gurnham and

^{*} Given averaging, as discussed below.

Becich, argued on the other hand that alkaline chlorination is not acceptable for steel industry wastes and will not produce results much better than the proposed 2.0 mg/l total and 0.1 mg/l free cyanide. It could, however, meet a 10 mg/l total, 2 mg/l simple, sewer discharge standard, (R.754). (Wisconsin Steel presently approaches 0.1 mg/l total cyanide at times using air-stripping, alkaline chlorination and sand filtration, (Ex. 32), although there is also some dilution of the cyanide-bearing waste streams, (R.758).)

Averaging

The averaging proposal before us here is in fact taken from another proceeding, R76-21, and was introduced only at the later hearings. The proposal was prepared by the Illinois Effluent Standards Advisory Group, with the support of the Illinois Institute for Environmental Quality and IEPA. In addition, its adoption was supported by essentially all the proponents and participants in the proceeding.

In short, the averaging proposal propounds a mechanism whereby an effluent standard is not an absolute discharge limit, but is rather a measure of required average performance over a monthly period based on composite samples. There are also provisions in the proposal to prevent environmentally damaging excursions beyond the monthly average, which might otherwise be mathematically allowed; daily composite samples cannot be more than twice the stated limit, and grab samples cannot exceed the limit by more than a factor of five.

Because treatment plants must operate under widely differing conditions, from day-to-day and from minute-to-minute, achievement of a very low concentration, absolute effluent limit requires over-design. To stay under an effluent ceiling, the plant must, on the average, discharge cyanide at a level far below the ceiling. Hence, we find the averaging proposal sensible, since it would eliminate the need to over-design a treatment plant, though this finding is limited here to cyanide effluents.

ECONOMIC IMPACT

The Economic Impact Study required by P.A. 79-790 was submitted by the Illinois Institute for Environmental Quality (IIEQ) on February 11, 1977.* Huff and Huff, The Economic Impact of Alternative Cyanide Standards in Illinois, IIEQ Doc. No. 77/03,

^{*} Exhibit E-4, the earlier study, Huff and Huff, Analysis of the Benefits and Costs of Alternative Cyanide Standards in Illinois, IIEQ Doc. No. 75/24 (1976), was withdrawn by IIEQ.

Proj. No. 20.065 (1976) [Ex. E-1]. The Study concentrated principally on costs and benefits associated with the various proposed effluent standards**, generally assuming water quality levels to be a direct function of effluent levels and emphasizing the proposed changes to Rule 703 (sewer discharge criteria) to the extent that costs were imposed upon sewer dischargers as a result of varying the potential effluent standards for direct dischargers, who would "pass along" stricter effluent standards in the form of stricter sewer discharge limits.

The Study's conclusions are summarized in Table 2-10, p.22. Because much of the testimony and argument regarding the Study concerned this Table (or its equivalent, Table 7-1), it is reproduced here:

Effluent Regulation	Annual Direct Costs,\$	Annual Projected Benefits
0.025 mg/l total cyanide - daily maximum	131,000,000 - 580,300,000	Protection of all waters for all use.
0.1 mg/l total cyanide - daily maximum	7,200,000 456,400,000	Protection of all waters ex- cept the Chicago-Illinois River System where loss of recreation valued at \$0 to \$62,000 occurs. Also, aes- thetic losses are possible.
0.1 mg/l total cyanide daily maximum with 0.3 mg/l total cyanide for Calumet STP	3,400,000	Protection of all waters ex- cept the Chicago-Illinois and Calumet River Systems where loss of recreation valued from \$0 to \$89,000 is possible. Aes- thetic losses are also possible.
0.1 mg/l simple cyanide - daily maximum	390,000	Loss of recreation on the Calumet and Chicago-Illinois River System valued from \$0 to \$700,000 is possible. Also, aesthetic and commercial fish- ing losses are possible.

^{**} The IIEQ Study pre-dated several proposals, including the IIEQ/ SAG proposal which introduced averaging concepts, and thus did not consider the effects of such later proposals. However, as noted above, averaging may in fact render the study more meaningful, as real effluent levels would be closer to those proposed.

Turning first to the costs associated with cyanide regulation, the study indicates that there are 13 major sources of cyanide which would be impacted economically by either enforcement of the existing standard (0.025 mg/l) or some other "tight" standard: three steel companies, eight refineries and two sanitary districts (MSDGC and Rockford) (Ex. E-1, pp.47, 42, 61, 59). Including those two sanitary districts, however, includes a significant number of smaller, indirect dischargers, many of them metal electroplating firms.

- In addition, there are also other minor, direct dischargers who are responsible for relatively low volume cyanide discharges (Ex. E-1, pp.75, 73). It should be noted, however, that smaller dischargers may be more seriously affected by a lower treatment standard; at an effluent standard of 0.025 mg/l (daily maximum) total cyanide, some small plating operations might have to cease operations altogether as the only possible compliance method.

In the steel industry, there are 8 significant cyanide sources: blast furnace and coke plant discharges from each of four plants. Of these, five discharge to MSDGC, one to the Calumet River, and two (already in compliance) to Horseshoe Lake. (The two complying sources, which are owned by Granite City Steel and discharge to Horseshoe Lake, were shown to be unusual cases.) Compliance costs for the steel industry in Illinois, for varying levels of Regulation, are set out in tables 5-7, 5-10, 5-12 and 5-13 of Ex. E-1. Compliance by all steel industry dischargers with existing regulations (including a sewer discharge limitation of 0.025 mg/1) would cost between \$56 million and \$506 million total (the latter indicating closure of all coke-dependent operations resulting from an inability to comply, and market unavailability of coke). As the effluent standard (and therefore, presumably, the sewer discharge standard) is relaxed, industry costs are more than proportionately reduced. Coke plant discharges to MSDGC, currently in violation of permitted 0.025 mg/l levels, would require capital investment of approximately \$5 million and operating costs in excess of \$100,000 annually, for compliance with a sewer discharge standard of 10 mg/l total and 2 mg/l readily releasable cyanide. Those figures constitute the majority of industry costs associated with a looser effluent standard for MSDGC's discharges.

Compliance with existing **standards** by petroleum refineries would cost in excess of \$8 million per year in annual operating costs, in addition to approximately 12 million in initial capital costs (table 5-6). In addition, considerable output would be lost. Again, as the standard is relaxed, compliance costs are more than proportionally reduced as treatment technology becomes more readily available. However, some costs remain even with a 0.3 mg/l effluent standard.

Compliance costs for sewer dischargers in the electroplating industry are presented in table 5-5 of the report. Costs for compliance with 0.025 mg/l (as now required when the receiving sanitary district is not itself meeting that same standard) would exceed \$66 million; at an effluent standard of 0.1 mg/l total cyanide, costs drop to \$0.09 million.

As the study notes, however, direct costs to dischargers of cyanide -- whether to waterways or to sewers and whether directly for compliance or due to lost output -- are not all the economic costs associated with a given level of regulation. The authors present macroeconomic costs, including indirect costs resulting from lost output and reduced employment, for various standards in table 5-15 (apparently the source of cost figures in table 2-10, These figures indicate, for example, that the reproduced above). lower expected indirect economic impacts of enforcing the existing 0.025 mg/l standard would exceed \$31.8 million; the range of possible indirect costs to the state goes considerably higher. As the standard is relaxed, and particularly as fewer cyanide sources are forced to cease operations as a compliance option, indirect costs decrease significantly (although not proportionately to direct costs).

Turning to benefit analysis, the Study's authors identified a considerable number of beneficial uses of Illinois waters potentially affected by varying levels of cyanide regulation, (Ex. E-1, § 6.1, table 6-1). For quantification purposes, however, the study concentrated on recreational/fishing activity and the possible gain or loss of such activity as cyanide levels in the receiving waters increased or decreased (as a function of effluent limits). In the table reproduced above, the figures shown in the "benefit" column are derived from this analysis.

There was some question as to the adequacy of such a limitation on benefit quantification, (See, eg., cross examination of the Huffs and Dr. Harberger by Mr. Park, IEPA). However, it should be noted that environmental benefit analysis is a new field, not easily given to any quantification. However, the willingness of Illinois citizens to pay for the use of clean water resources at varying levels of protection is a valuable approach. -18-

It is not, however, a complete approach. As the authors note, at three of the four regulatory effluent levels considered in table 2-10, aesthetic losses are possible, even though not quantifiable. In addition to recreation and aesthetics, the Board is constrained to consider the perhaps unquantifiable goals in § 2 of the Environmental Protection Act, III.Rev.Stat., Ch. 111-1/2, § 1002 (1975), that environmental quality be "restored, protected and enhanced".

As Republic Steel noted in its economic presentation and subsequent brief, a purely economic decision on cyanide regulation might indeed favor a standard looser than 0.1 mg/l total cyanide.* However, we find that such an argument could also rationally lead to the conclusion that a <u>far</u> more liberal standard should be chosen, or perhaps none at all, (See, eg., R.2210-11; see also R.2193, "I doubt that there is a benefit associated with fish life on these waterways that would warrant that kind of price [\$2 or \$3 million per yr].")

As required by § 27(b) of the Environmental Protection Act, we find that any standard for cyanide protective of aquatic life will have some "adverse economic impact on the people of the State of Illinois." The benefits of such protection (even though that same Act requires it) are not amenable to complete or adequate quantification, especially when compared to potential costs.

We feel, however, that the Institute's study presents sufficient data to choose a standard offering adequate environmental protection without requiring unnecessary control at excessive cost. An effluent standard of 0.1 mg/l total cyanide, given the averaging techniques for compliance measurement discussed above, was not even among the possibilities discussed in the study, but is the one we choose. It is less stringent than the 0.1 mg/l (daily maximum) total cyanide standard which the study would lead us to choose (from among the alternatives presented) and should involve considerably less compliance cost. On the other hand, it is more stringent than a 0.1 mg/l free cyanide standard, but will provide the necessary environmental protection, at a cost between .3 and 3 million dollars annually (although this cost may in fact be far lower, as a result of the separate provisions for the MSD Calumet Plant and sources that discharge to sewage treatment plants.

For a thorough discussion of optimal cyanide standards on an economic basis, see R.2214 and following (cross examination of Dr. Harberger).

THE REGULATION

The evidence before the Board justifies a change in the existing standards for cyanide. The reasons for the Board's decision follow:

- 1. Although much testimony was presented in the record that separate standards for free and total cyanide are scientifically justifiable, the Board has adopted a cyanide standard based on only total cyanide since the only generally accepted methods for determining cyanide are methods that measure total cyanide. The methods that estimate free cyanide are not generally accepted and do not necessarily reflect the potential toxicity of complex cyanides that may be present. For example, these methods do not measure iron cyanide complexes which may photodecompose and release free cyanide.
- The use of a single cyanide standard (i.e., total cyanide) will provide for rational compliance planning and monitoring.
- The general use water quality standard for total 3. cyanide is set at 0.025 mg/l in order to protect the warm water fish found in Illinois. Such a standard would be too high to protect cold water fish such as salmonids; however, although salmon are being stocked in Lake Michigan and trout are being stocked elsewhere in Illinois, these are not fish that are native to Illinois at the present time. Although some sub-lethal effects due to cyanide at this concentration may occur such as avoidance reactions or a reduction in fertility and fecundity, no fish kills due to cyanide would be expected. A general use water quality standard for cyanide (total) of 0.025 mg/l was supported in the record, as discussed above (see Toxicity section) and by public comments from the IEPA, USEPA, and others (PC# 36, 40, 41, 45).
- 4. The secondary contact and indigenous aquatic life water quality standard is set at 0.10 mg/l since much of the water in this river system is from effluents and because these waterways are already of limited recreational value. Although it was stated in the record that <u>free</u> cyanide concentrations near 0.10 mg/l (as CN) are eventually fatal

to a high percentage of fishes, it is thought that such high concentrations of <u>total</u> cyanide would be found only in limited reaches of these waterways as indicated in data presented by the MSDGC (R.1768) and that fish would probably avoid areas with toxic levels of cyanide. It is also unlikely that all the cyanide in a waterway would be present as free cyanide.

- 5. At present, the IEPA has the authority to determine if an apparent water quality standard violation falls within the margin of error inherent in the testing procedure. Hence, no separate provision that the "coefficient of variation shall not exceed 20% at the 0.025 mg/l level and the bias shall not exceed 10% of this level" has been set.
 - 6. No technically feasible and economically reasonable method of compliance with the existing 0.025 mg/l total cyanide effluent standard is available for all sources. Most dischargers will, however, be able to meet the effluent standards adopted at a reasonable cost in light of the environmental protection achieved.
 - 7. Complete assurance that free cyanide concentrations will <u>never</u> even <u>potentially</u> reach possibly chronic-damage levels in general wastwaters cannot be achieved without significant, unreasonable economic disruption, (realizing that chronic effects, and the levels at which they occur, are uncertain).
 - 8. An effluent requirement of 0.1 mg/l total cyanide will require removal of most toxic cyanide species and will require that the strongly complexed cyanides discharged be at levels low enough to prevent damage to downstream aquatic life.
 - 9. The MSDGC Calumet plant is allowed a higher effluent limitation than other sources since it receives cyanide effluents from steel mills and other industrial sources and generally has a higher cyanide influent loading than any of the other treatment plants in the state.

- 10. The use of averaging for effluent standard compliance testing will assure the necessary environmental protection, while allowing for good engineering practice and preventing uneconomical overbuilding of treatment facilities.
- 11. The standards adopted will not require unnecessary pretreatment by sewer dischargers. By eliminating certain of the permit requirements of Rule 703 (without limiting the authority of the receiving sewage system operator), we will eliminate unnecessary paperwork. The original purpose of the Sewer Discharge Criteria will still be met, while allowing localities to analyze and solve their own influent problems. (We have not taken into consideration any federal pretreatment requirements; obviously, our decision in this regard will have no effect on federal requirements.)
- 12. The sewer discharge standards should be sufficient to protect sewer workers from exposure to toxic concentrations of cyanide gas.

This Opinion constitutes the findings of fact and conclusions of law of the Board in this matter.

I, Christan L. Moffett, Clerk of the Illinois Pollution Control Board, hereby certify the above Opinion was adopted on the $\frac{1}{2}$ day of September, 1978 by a vote of $\frac{4}{2}$.

Clerk Christan

Illinois Pollution Control Board