STATIC COAL STORAGE--BIOLOGICAL AND CHEMICAL

EFFECTS ON THE AQUATIC ENVIRONMENT

by

Nathan A. Coward, Joseph W. Horton
Center for Lake Superior Environmental Studies
and Department of Chemistry
and
Rudy G. Koch, Robert D. Morden
Center for Lake Superior Environmental Studies
and Department of Biology

NERC-R-803937-02-0

Project Officer

Prepared For

PERSONNEL

## Biological - Fauna

| | | |
|---|---|---|
| Principal Investigator | - | Robert Morden, Ph.D. |
| Staff Assistant | - | Annette Morden |
| Assistant | - | Mary Ann Carter |

## Biological - Flora

| | | |
|---|---|---|
| Principal Investigator | - | Rudy Koch, Ph.D. |
| Staff Assistant | - | Lorraine Koch |

## Chemistry

| | | |
|---|---|---|
| Principal Investigators | - | Nathan Coward, Ph.D., Project Director |
| | - | Joseph Horton, Ph.D. |
| Staff | - | William Cook |
| | - | Thomas Markee |
| Graduate Student | - | Robert Stephenson |
| Undergraduate Assistant | - | Charles Kpea |
| Undergraduate Student | - | Harvey Johnson |

ABSTRACT

## A. BIOLOGICAL STUDIES

### 1. Vascular Macrophytes

A survey was made and representative samples of vascular macrophytes from the Superior, Wisconsin-Duluth, Minnesota Harbor were collected in August 1975 and stored in a frozen condition until processed. The processed samples were analyzed for environmentally sensitive metal concentrations by flameless atomic absorption spectrophotometry.

The effects of the presence of Western coal upon the growth patterns of Lemna minor L. was investigated. Lemna minor L. was grown in Lake Superior water in the presence of additional amounts of particulate coal. Temperature, humidity and light were controlled by the use of environmental growth chambers. Growth rates were determined by plant frond counts, and samples of Lemna were collected for metal uptake analyses.

Evidence was found to indicate that coal particulates, at certain concentrations, may diminish the growth of this aquatic plant. There also appeared to be increased metal uptake by the organism in the presence of coal particulates.

### 2. Benthos

A method using a recirculating water system is presented for rearing benthic organisms. A species of Chironomus was maintained in this system for seven generations. Heavy metals especially copper and lead were sequestered by Helobdella stagnalis. The benthic community in the region of the study changed little over the summer and the area of greatest community stability was located where higher levels of coal were found. The waters in the region of the ORBA coal dock facility were found to be mildly polluted as determined by the presence or absence of benthic indicator organisms as a measure of water quality and by using the diversity index of species found in the area as a measure of biologic stability.

## B. CHEMICAL STUDIES

The aqueous leaching of heavy metals from soft coal has been examined under a variety of conditions. Variables examined were pH, particle size, rate of flow, time of contact and oxygen or nitrogen atmosphere. Simple leaching of coal from Western mines with pure water does not remove large amounts of metal. Extended, successive releaches and mildly acid leaches

tend to remove greater amounts of metal from the coal. Leaching with a strong complexing agent removes relatively large amounts of metal from the coal. When placed in contact with water previously spiked with metal ions, the coal can actually act as an absorber and reduce the concentration of metal ions in solution. Hydrogen ion concentration has a marked effect on the release of certain metals.

Continuous flow and simple shaker leaching experiments correlate qualitatively with each other.

Considerable variation was found between Eastern and Western coal and also between different samples of Western coal.

CONTENTS

Chemical Research

## ACKNOWLEDGMENTS

# I. GENERAL INTRODUCTION

The use of low-sulfur western coal, as an acceptable energy source has been on the increase for several years. A transshipment facility, located at Superior, Wisconsin has been established to service coal shipped from western mines. The coal is transported by rail to Superior, transferred to an open air holding pile, and then from the holding pile to freighters (modified iron ore carriers) which carry the coal by water to its final destination where it is used as fuel for a steam-driven electrical power plant. Approximately three quarter of a million tons of coal per year pass through the transshipment facility.

The Center for Lake Superior Environmental Studies (CLSES), under contract with the Environmental Protection Agency, undertook a three phase study of the coal, and its possible effects on the immediate environs of the coal transshipment facility, the Superior, Wisconsin - Duluth, Minnesota Harbor and Lake Superior. The three phases of the study involved the following:

1. A survey of the vascular macrophytes of the area contiguous with the coal shipment facility, and a study of the uptake of metals, leached from the coal, by these macrophytes. Macrophytes, as an integral part of the local food chain, could serve as an entry point for high concentrations of environmentally sensitive metals which were derived from the coal.

2. A survey of the benthic organisms of the immediate area, and a rearing study of certain of these organisms, where the aquatic portions of the life cycles would be carried out in the presence of coal. Since benthic organisms are also an integral part of the food web of the area, the incorporation of deleterious metals, which were possibly derived from the transshipment coal, could be a serious problem.

3. A chemical study was undertaken to determine the levels of EPA sensitive metals in the western coals, and to investigate the factors which determine the mobilization of the metals from the coal matrix. Determination of these parameters would give an index as to the probable effects of the transshipment of millions of tons of coal upon the water quality and upon the aquatic flora and fauna of the immediate area.

   The chemistry study was performed to develop a reliable system and methodology for the determination of the leaching properties of coals, with respect to the mobilization and release of the environmentally sensitive metal content.

   Another portion of the duties of the chemistry research group was to provide routine chemical analyses for the two biological studies.

1

# II. BROAD GENERAL CONCLUSIONS

## A. BIOLOGICAL

### 1. Vascular Macrophytes

The survey of background levels of metal concentration in aquatic vascular macrophytes collected from the Duluth-Superior Harbor reveals considerable variation in different plants (see Table IV-A-2). This variation is particularly noteworthy for barium, lead and manganese. One species, an aquatic moss (*Fissidens grandifrons*, Brid.) appears to have the capacity to sequester manganese, lead and barium in quantities in excess of those of other aquatic macrophytes which were sampled.

The rearing study indicates that the addition of ground coal to lake water appears to initially augment *Lemna* growth. After 20 days, unfortified and low fortified (5.00 g of added coal) cultures of *Lemna* exhibit a decline in frond number, perhaps reflecting depletion of nutrients. Cultures with greater amounts of coal present (10.00 and 25.00 g of added coal) do not exhibit such declines of frond production, perhaps because the larger amount of coal present in the growth medium supplies larger amounts of nutrients. Examination of the growth rate constants suggests that there is a general decline in the growth rate of *Lemna* with time, irrespective of the presence or absence of added coal. Further work is needed to determine if this apparent effect is due to increased amount of deleterious materials leached from the coal, or merely due to other variables such as nutrient depletion, or simply crowding of individual organisms.

Within the limitations of this preliminary study, there is no overwhelming evidence to suggest that the presence of ground coal in the growth medium has a detrimental effect on the growth of *Lemna minor* L.

### 2. Benthos

The presence of coal appears to play a part in the stability of the benthic community. The increased stability is reflected in a greater number of organisms inhibiting a region. With more organisms there is a greater utilization of resources such as minerals in the area. Heavy metals appear to be sequestered by these organisms and thus a greater level is present in the food webs than before. If man is the highest level consumer in some of these food webs, caution should be used and conditions monitored to assure that these metals do not reach levels which are or will be detrimental to man.

B. CHEMICAL

1. Simple, slow percolation of relatively pure water (rain water or regular city water) does not leach heavy metals from western coal to any considerable extent.

2. Heavy metal leaching would be enhanced by:

   a. very acid leachant: The coal is naturally self-buffered, and leachant in contact with the coal approaches a pH of greater than 7 pH units (slightly alkaline). Additional acid, of the order of magnitude of approximately 4 liters of concentrated sulfuric acid per ton of coal would be needed to overcome the self-buffering capacity of the system and allow the mobilization of dangerous amounts of heavy metal ions. Of the metals studied, leaching of barium and manganese are most enhanced by high acid levels.

   b. strong complexing agents: Complexing agents such as EDTA (ethylenediaminetetraacetic acid) are capable of removing relatively large amounts of heavy metals from the coal. This implies that leach waters, heavily loaded with organic materials, might extract more heavy metals than pure water.

   c. successive releaching with pure water: The leaching of heavy metals from coal appears to be an equilibrium process. Continuous application of fresh, relatively metal-free water, will eventually remove rather large amounts of heavy metal from the coal. This is not postulated here as any real environmental hazard. Assuming that long term releaching could remove about $5 \times 10^{-6}$ g of manganese from 1 gram of western coal (based on the EDTA extraction work), a disaster which deposited about 50,000 metric tons of coal into the lake could contribute only about 0.3 ppb of Mn to 1 cubic kilometer of water. During EDTA extraction of western coals, manganese was extracted to the greatest extent. Other metals should give smaller effects.

3. There is excellent qualitative agreement between the results obtained from simple shaker extractions and those obtained from the more complex (and time consuming) continuous flow extractions. This would appear to be one of the most valuable results of this work as it establishes a reasonably firm basis for using shaker studies to survey the leaching properties of a variety of coal samples.

4. Western coal actually is an excellent sequesterer of metal ions at its naturally buffered pH of about 7.3. The spiked system uptake study shows that when the system is spiked with large concentrations of metal ions, the coal absorbs much more metal ion than it would release in equilibrium with distilled water. This suggests that if eastern (high sulfur) coal and western coal were to be used conjointly, storage of the western coal "downstream" from the eastern coal might be beneficial environmentally.

5. There appears to be significant differences in the leaching properties of different samples of western coal. This observation is in agreement with the work of Chadwick et al.[6] who did trace metal analyses on cores taken

from a typical western coal seam.  This implies that future leaching work should probably be based on a rather extensive and statistically significant sampling scheme.

# III. FUTURE RESEARCH POSSIBILITIES

## A. BIOLOGICAL

### 1. Vascular Macrophytes

*Fissidens grandifrons* Brid., apparently has the ability to sequester large quantities of certain heavy metals. It would seem most useful to test other samples of this moss, as well as to examine other aquatic mosses to determine if mosses have greater potential than other aquatic vascular macrophytes to serve as sequestering agents, and thus serve as bioassay organisms for heavy metals.

Also, the problem of growth of *Lemna* sp. should be investigated more completely to determine whether a very simply handled and cultured aquatic macrophyte could serve as a bioassay organism for these purposes.

Additional monitoring of plants which can absorb these environmentally sensitive materials and insert them in the food chain which can ultimately lead to man remains a necessity.

### 2. Benthos

Future research should concentrate on studies conducted in the laboratory. This study has shown that benthic organisms are able to be reared under laboratory controlled conditions for generations. By exposing these organisms to known levels of introduced material, their effect can be assumed by monitoring the level of time of the various growth stages of the organism and the mortality of the colony.

## B. CHEMICAL

The most obvious extension of this work would appear to be the development of a coal field survey technique. This would involve; (1) field geological sampling from the coal field, (2) trace metal leaching tests in the laboratory and (3) analysis of other coal parameters of interest.

The "on site" sampling would be a major project in itself. It would require a trained field geologist who would obtain proper "in situ" samples from the coal field. It is assumed that samples would be taken from selected test holes along the entire coal seam.

The laboratory leaching studies would involve deionized water leaching and EDTA (ethylenediaminetetraacetic acid) leaching of the samples. Shaker tests using 200 grams of ground and sieved coal for each liter of leachant would be used. Samples would be analyzed using flameless atomic absorption with a roulette type automatic sample feeder. The atomic absorption output could be interfaced with a digital computer for ease in data reduction.

The laboratory leaching work should be standardized as much as possible so that the method would give reliable comparisons between different coal seams.

The problem of filter absorption of trace metals during sample preparation has not been solved. Research on this problem should definitely be continued.

IV.  BIOLOGICAL RESEARCH

A.  VASCULAR MACROPHYTES

1.  Background Levels of Heavy Metals in Harbor Aquatic Macrophytes

a.  Introduction--
     Heavy metals are frequently sequestered by plants, and if these plants
are important in the food chains of an area, they may serve as a source for
the introduction of the same heavy metals into higher level consumers.  In
examining the effect of the coal transshipment facility on the addition and
dispersion of heavy metals throughout the Superior-Duluth Harbor, it was nec-
essary to obtain some preliminary estimates of background levels of the met-
als under study in the aquatic vascular macrophytes which were present in the
harbor.

b.  Experimental Procedure--
     Samples of the aquatic macrophytes were collected in August 1975 from
areas in the Superior-Duluth Harbor near the coal transshipment facility con-
struction site.  The samples were rinsed with distilled water to remove sur-
face contaminants and then placed in acid-washed polypropylene bottles.  The
specimens were then frozen and stored in a frozen condition until processed
for metal analyses.

     Representative portions of the stored specimens were oven dried to con-
stant weight, digested in an ignition bomb by means of ultrapure nitric acid,
and then metal concentrations were determined by flameless atomic absorption
spectrophotometry.  Sample preparation was as described in Section V-B-7 of
this report.

c.  Results and Discussion--
     Results of the preliminary population survey are shown in Tables IV-A-1
and IV-A-2.  Table IV-A-1 is a record of the species collected, and the por-
tion of the plant which comprises the analytical sample.  Table IV-A-2 gives
the results of the various analyses for the metals under consideration.

     Results demonstrated that the different species concentrated the differ-
ent metals not only in differing amounts, but also that the various parts of
the plant had differing levels of metals present.  Perhaps most unusual were
the levels of lead and manganese sequestered by the aquatic moss, *Fissidens
grandifrons* Brid.  These high levels are worthy of further study, particular-
ly to determine if the concentration of these metals is a result of the sub-
strate from which they were collected, or if the species under consideration
has an unusual facility for sequestering these metals (lead and manganese).
Also noteworthy are the relatively low levels of metals in wild rice (*Zizania*

7

*aquatica* L.), which is one of the few aquatic macrophytes in the area now directly eaten by man.

Many of the other species investigated may be eaten by ducks or fish, and in turn consumed by man (Fassett, 1960). Thus, the levels of environmentally sensitive metals in these aquatic vascular macrophytes may eventually be a matter of concern to the region.

d. Recommendations--
A continual monitoring program of selected plant species in the harbor would be a useful tool in judging the role of plants in heavy metal uptake within the Superior-Duluth Harbor ecosystem. The high levels present in the aquatic moss *Fissidens grandifrons* needs further study.

## 2. Effects of Particulate Coal on *Lemna minor* Growth

a. Introduction--
Many metal ions have been found to be essential for normal plant growth and function. Manganese was found by early workers (Epstein, 1972) to be required. The role of many such elements has been shown in enzyme activation, regulation or stimulation. Epstein has reported (1972) that, in addition to its primary function, manganese served as an activator of some enzymes by substituting for magnesium in certain phosphate transferring enzymes. The same author also reported that manganese, if present in high concentration, induced iron deficiency in some plants. Treshow (1970) demonstrated that certain trace elements and/or alien metal ions could induce metal deficiencies or be directly toxic to plants.

In view of the relatively low levels of nutrients and dissolved ions in the waters of Lake Superior, addition of even small amounts of coal, from which a variety of materials can leach, is potentially disruptive. The addition of coal particles to the aquatic environment would presumably have an effect on the aquatic vascular macrophytes, depending on the amount of coal present. The presence of coal could result in increased growth (through the addition of nutrients) or increased environmentally sensitive metal uptake from the coal-enriched surroundings (which could result in growth inhibition at excessive metal levels).

The second phase of this aspect of the study was to investigate the feasibility of studying heavy metal uptake in vascular aquatic plants. Initial efforts were directed toward selecting a study species and determining a potentially useful procedure. Within the limitations of the budget and time allocation of the first year (and in anticipation of further work in subsequent years), it was possible to make only preliminary attempts to answer the major questions of this year. Initial efforts were focused upon a study of the effect of coal upon *Lemna minor* L. This study was to serve the dual purposes of: (1) determining laboratory techniques for the rearing of *Lemna minor* L. in the presence of coal, (2) providing a first approximation of the relationship between the presence of coal particles and *Lemna* growth.

*Lemna minor* L. was selected as the plant for these initial studies because of its small size, relatively rapid growth and structural simplicity.

TABLE IV-A-1.  SPECIES AND HABITATS MONITORED FOR BACKGROUND LEVELS OF HEAVY
METALS IN THE DULUTH-SUPERIOR HARBOR AREA.

| Sample Number | Taxon | Portion Analyzed | Habit |
|---|---|---|---|
| 1 | Lemnar minor L. | Whole Plant | Free-Floating |
| 2 | Fissidens grandifrons Brid. (a moss) | | Attached to Wood Piling |
| 4A | Bidens cernua | Stem | Emergent |
| 4B | | Leaves | |
| | | Flower | |
| 5 | Ceratophyllum demersum L. | | Submerged |
| 7 | Scirpus validus Vahl. | Rhizome | Emergent |
| 8 | | Root | |
| 9 | | Leaf | |
| 10 | Nuphar variegatum Engelm | Whole Plant | Floating Leaved |
| 11 | Zizania aquatica L. | Sead | Emergent |
| 12 | | Root | |
| 13A | | Stem | |
| 13B | | Leaf | |
| 14 | Bidens beckii Torr. | Leaf | Submerged |
| 15 | | Root | |
| 16 | Sparganium chlorocarpum Rydb. | Root | Emergent |
| 17 | | Flower | |
| 18 | | Leaf | |
| 19 | Sagittaria latifolia Willd. | Root | Emergent |
| 20 | | Leaf | |
| 21A | | Stem | |
| 21B | | Flower | |

9

TABLE IV-A-2. CONCENTRATION OF METALS (ppm) IN CERTAIN DULUTH-SUPERIOR HARBOR PLANTS (BY DRY WEIGHT)

| Sample | As | Ba | Cd | Cr | Co | Cu | Pb | Mn | Mo | Ni | Se | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 237 | 0.4 | 4.9 | 6.5 | 15 | 29.4 | 5000 | 1.5 | 23 | 0.8 | 5 | 16 |
| 2 | 11 | 528 | 0.8 | 14.8 | 15.0 | 32 | 198.8 | 15400 | <1.5 | 11 | <0.1 | 8 | 9 |
| 4A | <1 | 25 | 0.2 | 0.9 | 0.7 | 12 | 4.7 | 653 | -- | 39 | -- | -- | 10 |
| 4B | <1 | 95 | 0.1 | 1.8 | 4.6 | 17 | 2.2 | 2080 | -- | 3 | -- | -- | 8 |
| 4C | <1 | 23 | 0.1 | 0.9 | 1.0 | 13 | 2.0 | 1170 | -- | 3 | -- | -- | 5 |
| 5 | 5 | 604 | 0.8 | 4.1 | 5.7 | 106 | 30.5 | 746 | -- | 11 | -- | -- | 11 |
| 7 | -- | 4 | -- | <0.1 | -- | 2 | 0.4 | 102 | -- | 2 | -- | -- | 3 |
| 8 | 12 | 20 | 0.5 | 1.9 | 6.9 | 7 | 11.5 | 2040 | -- | 6 | <0.1 | -- | 10 |
| 9 | <1 | 78 | 0.1 | 0.5 | 1.9 | 2 | 3.3 | 962 | 1.2 | 4 | 0.3 | <4 | 3 |
| 10 | <1 | 367 | 0.3 | 1.7 | 5.0 | 28 | 78.8 | 618 | <2.1 | 79 | 1.2 | <5 | 23 |
| 11 | <1 | <7 | 0.1 | 0.4 | 8.8 | 11 | 2.4 | 250 | -- | 4 | 1.6 | <5 | 8 |
| 12 | 5 | 50 | 0.1 | 2.5 | 5.4 | 9 | 8.8 | 573 | -- | 14 | -- | -- | 9 |
| 13A | 8 | 176 | 0.5 | 11.7 | 9.0 | 208 | 23.5 | 781 | -- | 59 | -- | -- | 22 |
| 13B | <1 | 87 | 0.3 | 3.2 | 5.5 | 31 | 13.3 | 353 | -- | 12 | -- | -- | 18 |
| 14 | <1 | 112 | 0.2 | 1.3 | 2.3 | 8 | 3.8 | 1250 | -- | 2 | -- | -- | 4 |
| 15 | 6 | 95 | 0.2 | 2.5 | 3.5 | 24 | 10.4 | 1570 | -- | 2 | -- | -- | 6 |
| 16 | 6 | 64 | 0.1 | 1.8 | 5.8 | 10 | 11.8 | 1520 | -- | 35 | -- | -- | 7 |
| 17 | <1 | <3 | 0.1 | 0.3 | 2.4 | 3 | 1.4 | 90 | -- | 1 | -- | -- | 7 |
| 18 | <1 | 50 | 0.1 | 0.8 | 2.8 | 18 | 23.1 | 254 | -- | 29 | <0.2 | -- | 8 |
| 19 | 10 | 479 | 0.4 | 5.5 | 1.0 | 18 | 15.9 | 479 | -- | 5 | -- | -- | 21 |
| 20 | <1 | 18 | 0.1 | 0.4 | 1.6 | 8 | 1.8 | 261 | -- | 6 | -- | -- | 5 |
| 21A | <1 | <9 | 0.2 | 0.6 | 1.4 | 36 | 3.1 | 263 | -- | 6 | -- | -- | 11 |
| 21B | 1 | <4 | 0.1 | 0.6 | 0.6 | 85 | 4.5 | 168 | <1.2 | 1 | 0.2 | <3 | 6 |

*Lemna minor* L. produces new daughter fronds from pockets at the base of the parent plant and these new plants may, in turn, produce daughter fronds even before they are detached from the original parent. Growth may be followed by counting these fronds, a procedure which has proven to be quite reliable (Hillman, 1961).

Another factor which lead to the adoption of *Lemna minor* L. as the test organism was the extensive experimental literature on *Lemna* sp. (see Hillman, 1961, for a review of the description and use of the Lemnacae in experimental procedures).

b.  Experimental Procedures--
Field collection of *Lemna minor* L. were made from indigenous populations, rinsed with deionized water to remove any gross contamination, and reared in acid-washed aquaria using Lake Superior water as a culture medium. From the above culture, groups of twenty-five (25) unattached *Lemna minor* L. fronds (without daughter fronds) were removed, rinsed three times with deionized water and placed in 600 ml acid-washed polypropylene beakers which contained 300 ml of Lake Superior water.

A portion of Western Coal No. 1 (see Section V-B-1) was ground in the Wiley® mill and then added to the beakers of *Lemna minor* L. culture. The amount of coal added to each beaker was 5.00 g, 10.00 g or 25.00 g. Triplicate sets of *Lemna minor* L. culture samples were prepared with each size of coal adduct.

The beakers were covered with acid-washed glass plates and placed in an environmental chamber in which temperature was held constant at 25°C. A sixteen-hour light period at an intensity of 1200 foot-candles (12,900 lumens/ square meter) alternated with eight hours of darkness. Growth was allowed to proceed for 21 days. Water lost through evaporation was replaced with deionized water.

The lake water culture medium was sampled prior to the start of the growth chamber study, and all growth media which had been in contact with coal were sampled at the end of the 21 day growth period. The samples were acidified with ultrapure nitric acid and were stored in acid-washed polypropylene bottles until analysis for metal content were performed. In addition, samples of the *Lemna minor* were taken from the population for metal analyses at the initiation of the run, as well as from each culture at the conclusion of the test period.

At the end of the growth, the *Lemna* were harvested (after counting), dried to constant weight, and the residue analyzed for its metal content (see Section V-B-7 for sample preparation and analysis).

Individual counts of all plant fronds (as previously described) were made at intervals, to determine growth rates and to observe the plant growth response to the presence of coal derived materials in the Lake Superior water growth medium.

11

c. Results--

Initial efforts in the laboratory phase of this study were directed toward establishing procedures for the culturing of *Lemna minor* L. in media which was fortified by the addition of ground coal in various concentrations. As a result, time was not available for the adequate retesting of the results tabulated in this report. Inspection of these data showed no consistent patterns. Because of the preliminary nature of the data (and the inherent variance), it was felt that no statistical tests were warranted.

A summary of the growth response of *Lemna minor* to varying concentrations of ground coal present in the lake water medium is presented in Table IV-A-3.

TABLE IV-A-3. Growth of *Lemna minor* L. in Coal Fortified Lake Water (Average Frond Counts of Three Trials)

| Medium | Number of Fronds by Day | | | | | | | | |
|--------|---|---|---|---|---|---|---|---|---|
| | 1 | 3 | 7 | 10 | 13 | 16 | 20 | 22 | 23 |
| Lake Water, No Coal Added | 25 | 52 | 128 | 184 | 215 | 243 | 140 | 147 | --- |
| Lake Water, 5.00 g Coal Added | 25 | 61 | 146 | 182 | 191 | 218 | 169 | 193 | --- |
| Lake Water, 10.00 g Coal Added | 25 | 71 | 126 | 163 | 195 | 241 | 232 | --- | 267 |
| Lake Water, 25.00 g Coal Added | 25 | 61 | 148 | 188 | 200 | 235 | 228 | --- | 256 |

Table IV-A-4 presents the growth rate constants as determined from frond counts (Hillman, 1961). The first three days are omitted on the assumption that they represent more nearly the conditions existing in the original culture than that of the experimental media. Frond count data after 16 days are also omitted from this table since frond counts for unfortified lake water and water with 5.00 grams of added coal are declining--perhaps due to lack of nutrients.

TABLE IV-A-4. Growth Rate Constants for *Lemna minor* L. in Coal Fortified Lake Water (Average of Three Replicates)

| Medium | Interval (Days) | | | |
|--------|-----|------|-------|-------|
| | 3-7 | 7-10 | 10-13 | 13-16 |
| Lake Water, No Coal Added | .098 | .053 | .023 | .018 |
| Lake Water, 5.00 g Coal Added | .095 | .033 | .007 | .019 |
| Lake Water, 10.00 g Coal Added | .083 | .037 | .026 | .031 |
| Lake Water, 25.00 g Coal Added | .096 | .035 | .009 | .023 |

Table IV-A-5 presents data for the average metal concentration in the lake water culture media (with and without coal) at the beginning and end of the 21 day growth test with *Lemna minor*. Table IV-A-6 contains data for the average metal concentration in the *Lemna* grown in the above culture media. Certain metals (such as barium) seem to be increasingly sequestered from the media with increasingly higher amounts of added coal. Others (Zn, Pb) show greater levels of accumulation at intermediate concentrations of coal additive. However, other metals (cobalt, copper, manganese) exhibit no marked trends.

d. Recommendations--

Preliminary work suggests that *Lemna minor* is a useful plant to study uptake of heavy metals. It does not require elaborate culture techniques and its small size allows smaller (and less expensive) culture facilities.

Although the work reported above reflects only a first approximation in examining the role of plants in heavy metal uptake from coal particles, there is evidence that coal particulates may, in certain concentrations, diminish the growth of an aquatic plant. In addition, there appears to be increased uptake in the presence of coal particles, but considerably more work remains to be done in understanding the nature and extent of this uptake before assessing its significance.

The use of unfortified lake water alone as the medium poses some difficulties since the levels of available nutrients is low. However, within the harbor ecosystem, uptake of these metals by aquatics is likely to be limited by similarly low nutrient levels. Further work to relate uptake with the nutrient level of the growth media would be useful.

Another variable which needs to be examined is the effect of water currents and circulation on rate of metal from the coal. The above work involved only static testing, simulating coal accumulation at the bottom of the water column. Since water currents are present, much coal, especially fine particles, could be held in suspension for periods of time, increasing the likelihood of leaching. Related to this is the need to better understand the effect of particle size upon leaching rate which should be reflected in uptake rates.

The significance of metal concentrations reported in Table IV-A-6 must be interpreted with extreme caution. It is hard to explain the variance present without a much greater understanding of the behavior of each metal tested. The possibility of error in metal determinations, particularly due to the small amount of tissue available, must be considered.

TABLE IV-A-5. HEAVY METAL CONCENTRATION, ppb, IN THE WATER CULTURE MEDIUM BEFORE AND AFTER A 21 DAY Lemna minor GROWTH PERIOD WITH VARYING CONCENTRATIONS OF COAL ADDITIVES (AVERAGE OF THREE REPLICATES).

| | As | Ba | Cd | Cr | Co | Cu | Pb | Mn | Mo | Ni | Se | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Initial Lake Water Levels | 0.0 | 3.3 | 0.00 | 0.0 | 0.0 | 1.30 | 0.70 | 0.4 | 0.00 | 0.7 | 0.20 | 0.0 | 0.4 |
| Water Levels After 21 Days of Growth | | | | | | | | | | | | | |
| No Coal Additive | 0.0 | 0.0 | 0.08 | 0.1 | 0.0 | 1.80 | 0.00 | 0.1 | 0.00 | 20.5 | 0.30 | 0.0 | 1.4 |
| 5.00 g Coal Added | 0.0 | 1.1 | 0.05 | 0.1 | 0.2 | 0.10 | 0.30 | 0.1 | 0.60 | 3.7 | 0.00 | 1.0 | 1.9 |
| 10.00 g Coal Added | 0.1 | 2.2 | 0.05 | 0.0 | 0.2 | 1.60 | 0.10 | 1.1 | 2.32 | 0.0 | 0.00 | 1.9 | 0.8 |
| 25.00 g Coal Added | 0.0 | 3.3 | 0.07 | 0.1 | 0.2 | 1.10 | 0.06 | 1.0 | 2.10 | 7.1 | 0.95 | 0.0 | 0.1 |

14

TABLE IV-A-6. HEAVY METAL CONCENTRATION, ppm (BY DRY WEIGHT BASIS) IN Lemna minor L. GROWN IN DIF-
FERING LEVELS OF COAL-FORTIFIED MEDIA (AVERAGE OF THREE REPLICATES).

| | As | Ba | Cd | Cr | Co | Cu | Pb | Mn | Mo | Ni | Se | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Initial Concentrations in Lemna | 0.30 | 10.0 | 1.9 | 0.5 | 0.30 | 40.0 | 0.8 | 33.0 | 1.6 | 8.0 | 8.0 | 4.0 | 50.0 |
| Final Concentrations in Lemna | | | | | | | | | | | | | |
| Lake Water, No Coal Added | 0.70 | 11.0 | 0.4 | 0.4 | 0.70 | 14.0 | 41.2 | 257.0 | 3.4 | 9.0 | 0.5 | 8.0 | 17.0 |
| Lake Water, 5.00 g Coal Added | 0.80 | 161.0 | 0.7 | 0.7 | 2.20 | 20.2 | 4.1 | 117.0 | 4.3 | 10.0 | 0.6 | 11.0 | 28.0 |
| Lake Water, 10.00 g Coal Added | 0.80 | 210.0 | 0.8 | 2.9 | 1.05 | 81.0 | 7.7 | 268.0 | 4.2 | 19.0 | 0.7 | 11.0 | 42.0 |
| Lake Water, 25.00 g Coal Added | 1.33 | 114.0 | 1.6 | 0.8 | 1.30 | 21.0 | 16.0 | 143.0 | 6.7 | 46.0 | 13.9 | 17.0 | 62.0 |

## 3. Literature Cited

Epstein, E. 1972. Mineral Nutrition of Plants: Principles and Perspectives. John Wiley and Sons.

Fassett, Norman C. 1960. A Manual of Aquatic Plants. University of Wisconsin Press.

Hillman, W. S. 1961. The Lemnaceae, or Duckweeds. Bot. Rev., 27:221-287.

Treshow, M. 1970. Environment and Plant Response. McGraw-Hill, Inc., New York.

# B. BENTHOS

## 1. Introduction

The study of benthos is concerned with substrate organisms, both plant and animal, that live in or on the bottom of a body of water. In the St. Louis River, these organisms are important in the ecosystem as sources of food either directly or indirectly for higher organisms such as fish, birds and man (Anderson and Smith, 1971). Thus the stability and the functioning of this portion of the ecosystem has far ranging effects upon a variety of organisms. Certain substances may accumulate either temporarily or permanently in these organisms. These substances may be later found stored in higher members of the food chain of the animal kingdom at an increased level because of the high number of organisms consumed as food. The increased concentration of certain substances, which can in some cases reach many thousand fold over the concentration originally found in the waterway, may interfere with normal physiological functions within the higher level consumers. Therefore, it is becoming increasingly apparent that the chain of events leading from benthic organisms to the highest member of the food chain needs to be further investigated in greater detail. This study identifies the benthic organisms which will be exposed to material leached from coal to coal dust as a result of storage close to a water system. It also shows concentrations of heavy metals found in some of the benthic organisms and it describes how some benthic organisms can be reared under laboratory conditions so that future laboratory controlled experiments can be performed. Also described are various aspects of the natural history of benthic organisms which were kept in culture.

## 2. Methods

Field Sampling Techniques--

The biological research group at the University of Wisconsin-Superior sampled four areas in the region of the ORBA Coal Dock facility and two areas of the existing Riess Coal Dock three times during 1975. The sampling dates were July 9, August 9 and September 29, 1975. All benthic samples were collected with a 23 cm x 23 cm Ponar dredge. Three samples were taken from each of the six areas. The three replicate sites were generally within 50 yards of each other and were visually selected to represent the general conditions found within the area. All samples were placed in five quart plastic containers and frozen immediately upon return to the laboratory. These samples were kept frozen until sieving and then the organisms were sieved with a 30 mesh screen and preserved in 70% ethyl alcohol until they were identified using a dissecting microscope. Identification of organisms to species, where possible, was accomplished using the following keys: Burch, 1972 and 1973; Mason, 1973; Edmondson, 1959; Pennak, 1953; Eddy and Hodson, 1961; Needham and Needham, 1962; Williams, 1972; Klemm, 1972; Brown, 1972; and Holsinger, 1972.

Laboratory Rearing--

The initial stock organisms of *Chironomus* sp. were collected from the substrate in the St. Louis River July 21, 1975. These organisms were transported to the laboratory in five quart containers and here the Chironomids freed themselves from the substrate and entered the water column. These organisms were then transferred to the rearing chambers with a wide apparatus eye

17

dropper.

Rearing Chambers--
     The rearing chambers were 3" x 8" culture dishes in which a hole 20 mm
in diameter was drilled one inch from the top and was fitted with a #3 one-
hole neoprene stopper in which was inserted an 8" L-shaped glass tube (see
Figure IV-B-1). This tube formed an outlet to the rearing chamber. The end
of the tube which protruded into the rearing chamber was lightly fitted with
glass wool to prevent culture organisms from escaping. Recirculated water
passed through this outlet tube and into a five gallon aquarium which was lo-
cated directly beneath (Figure IV-B-1). This aquarium held the bulk of the
recirculated water used for the rearings.

     Water entered the rearing chamber by being elevated from the five gallon
aquarium mentioned above by a continuous stream of air bubbles passing through
a 10" culture dish inlet tube. The temperature of the incoming water could be
regulated by controlling the rate of air flow through the inlet tube by ad-
justing the air valve. A temperature of 20.5 + 0.5°C (monitored by a contin-
uous recording thermometer) was maintained for all chironomid colonies. Wa-
ter used for the rearings was Lake Superior water obtained from the Environ-
mental Research Laboratory, Duluth, Minnesota.

Temperature Control Tank--
     To control the temperature of water in the five gallon aquarium which in-
fluenced the temperature in the culture dishes, the five gallon aquaria were
placed in a thirty gallon aquarium tank which had connections to hot and cold
water (not shown in Figure IV-B-1). By regulating the flow of water from each
tap a uniform (+ 1°C) temperature could be maintained both during the summer
and winter months.

*Chironomus* sp.--
     Egg Stage--Eggs were deposited by the female at the surface of the water
in a gelatinous mass with a varied egg pattern. Some contained a single
strand of eggs evenly deposited in a spring-like coil and some had a more ran-
dom egg pattern. The number of eggs laid varied among the females but usually
the number was between 100-350. Based on ten colonies reared at 20.5 + 1°C,
it takes 5.1 days to hatch.

     Larva Stage--Soon after hatching the larvae began to build tubes which
were open at both ends and in which the larvae spent the majority of their
larval and pupal life. As the larvae grew material was added to this tube to
compensate for the increase in body size. In nature this tube is usually
built of algae, fine silt and small sand grains but in the laboratory without
extraneous material the tube was constructed mostly of fecal material.

     Growth from the time of hatching to pupal formation based on ten colonies
took 21.9 days. The first day after hatching the larval length ranged from
1 mm to 1-1/2 mm; the third day from 3 to 6 mm; the seventh day 5 to 8 mm;
the ninth day 8 to 10 mm; the twelfth day 10 to 15 mm, the sixteenth day from
10 to 20 mm. Because much of the larval life is spent inside their tubes it
is difficult to predict with certainty the number of larval instars. However,
it may be predicted, by indirect means, to be approximately six. Because of

the range in size throughout the growth period, the size difference appears to be a result of dimorphic differences among the larvae. The size may be the difference between future males and females. This accounted for the size difference among larvae of the evergreen bagworm, *Thyridopteryx ephemeraeformis* (Morden, unpublished data) which also had a case which enclosed the larvae.

Laboratory stress factors can influence the rate of growth of the larvae. One factor was stagnation. Several attempts were made to rear the larvae using two quart non-circulating rearing chambers. In all cases the chironomids failed to complete one life cycle with most colonies failing to grow past the fourth instar.

Another factor was diet. The food fed to the larvae influenced the growth rate as well as their general vitality. Two kinds of food were fed to the larvae. The chironomids were able to complete a life cycle using either Red Star(R) instant blend active dry yeast or Tetramin(R) staple food, a widely distributed tropical fish food. However, there was slower growth and higher mortality when yeast was used instead of Tetramin(R). The data on life cycles were based on colonies which were fed Tetramin(R). This food was placed in the rearing chamber each day. The amount fed was just what the colony would consume in thirty minutes.

Larvae in the fourth instar were transferred to tap water. Activity soon became slower and the colony failed to survive beyond the fourth day in the tap water even though food was supplied. This may have resulted from chlorine found in tap water.

Water from a well which was drilled on campus during the fall of 1975 was used and the chironomids were able to complete a life cycle although mortality was higher than when Lake Superior water was used. Mortality in this colony approached 90% compared to the 10% reared under optional conditions. This well water was later tested and found to be high in salts.

The hemaglobin pigment found in some Chironomids is red and the presence in the insect can be observed by visual inspection. During the first instar no red pigment can be seen. During the second instar the larvae change from pink to red and by the third instar the larvae blood appears to be fully hemaglobinized.

The larvae swim by an interesting twisting motion of one part of its body on another. Following a "S" shaped pattern, the posterior end of the larvae curls up in a twisting motion and passes over the head. As this happens the anterior half of the body flips quickly downward giving the "lift" necessary for swimming.

When healthy larvae are not swimming they remain in their tubes with the anterior half of the body extending from the tube and swaying back and forth. This motion may aid the larvae in obtaining oxygen by permitting more water to pass over the body surface. This motion in clearer water, however, may attract fish and thus would not be as beneficial to the chironomid.

19

Pupa Stage--The pupa stage, based on ten colonies at 20.5-1°C, lasts for 2.1 days. When the larvae change to the pupa stage the head capsule become larger and more defined and possess two small white tufts. The pupae are less active then the larvae but retain some motility as they can tumble through the water. The size of the head capsule in relation to the body becomes noticeably greater when the larvae change to the pupal stage.

Just before pupation the larvae closes the ends of its tube and then develops to the pupa stage. However, it is not necessary to change within the tube as some successfully completed the transformation in the laboratory outside the tube. Just before the adult emerges from the pupal case, the pupa is found at the surface of the water.

Adult Stage--The adult emerges from the pupal skin by pulling itself out through the split in the thoracic segment and then flies away. Based on ten colonies, from the moment until the first eggs are deposited takes 5.4 days.

The females are easily distinguished from the males by the antennae. The males' antennae are feathery or plumose while the females' antennae are simple and stylate.

The total duration from egg stage through egg stage based on the ten colonies at 20.5 $\pm$ 1°C was 32.4 days. The percent mortality of the colonies from the egg stage to the adult stage was approximately 10%.

## 3. Results

### Benthic Indicator Organisms--

Indicator organisms are used to provide a relatively fast and easy means for attempting to classify the environmental quality of an area.

Benthic organisms which normally do not tolerate toxic pollution are: *Physa* snails and one was found at site six (The C. Reiss Coal Company site) in the spring sampling. Sphaerid clams were generally found in the shallow sites during the entire collecting season. Red chironomids were generally present in all areas sampled. Worms, leeches, *Asellus* and molluscs are very susceptible to lead, zinc and copper and members of these taxa were found within the collecting area (Thomas, Wilcox and Goldstein, 1976).

### Diversity Index--

A more stable and predictive assessment of environmental stability and water quality is the concept of species diversity. Its shortcoming is the inability to reflect accurately the biomass and the individual species present.

Because of the uniform size of the samples taken from each collecting site the following equation was used to calculate the diversity index (D.I.).

$$D.I. = \frac{N^2}{\Sigma n_1^2 + n_2^2 + n_3^2 \ldots n_x^2} \qquad \text{Kaill and Frey, 1973}$$

20

The total number of organisms collected from a site is squared $(N^2)$ and this number is divided by the sum of the squares of each species $(n^2)$. A higher number reflects a greater diversity among the species and this usually indicates a greater species interaction and greater ecological stability.

Using the above formula, values close to 10 indicate clean water and a stable environment. Values close to 1 indicate that the number of species interaction is generally reduced while intermediate values indicate a moderate degree of interaction and stability.

All sites indicate little species interaction. However, one site is clearly more stable than the others during all sampling periods. This was site six, a shallow, coal-rich area found at C. Reiss Coal Company site (see Tables IV-B-4 through IV-B-6).

Diversity Index Relationships--
    t-Test--Because the data was symmetrically matched by site location during the collecting period a t-test (McCall, 1975) was performed on the D.I. to see if any significant differences existed between the spring samples, the summer samples and the fall samples. This analysis should show changing levels of species interactions among the sites during the collecting period.

As seen from Table IV-B-1 the greatest difference observed was between the summer sampling and fall sampling but the assumption that a change occurred can be made with only 29% certainty. There was no significant change between spring and summer samples. Therefore, the change in the relative stability of the environment among the sites during the seasonal period of active growth for organisms is at most only extremely slight.

Correlation Analysis--
    A correlation using the D.I. was performed on the data to see if community stability was different among the sites when comparing shallow and channel depths and between coal and non-coal environments.

From Table IV-B-2 the t values exceed the critical values at the .05 level with seven degrees (n-2) of freedom. Therefore, a significant difference does exist at the .05 level. There is a greater diversity found in coal areas than non-coal areas and there is greater diversity in shallow areas compared to channel depths.

Heavy Metal Concentrations--
    The heavy metals examined in the laboratory were found in *Helobdella stagnalis* at all sites during the collecting period.

The test organisms were collected during 1975, identified in the laboratory and stored in 70% ethyl alcohol. Samples were later dried in a vacuum oven for 5 hrs at 70°C. If not used immediately samples were stored in a desiccator. Sample weights were determined, then organisms were placed in Parr bomb and digested. Approximately 2 ml of ultrapure nitric acid was used for each digestion. The digested samples were then diluted to a predetermined volume (m-1 through m-8 to 20 ml) and analyzed by atomic absorption methods. Results are found in Table IV-B-3. For methods refer to Section V-B-7.

21

To obtain enough weight per sample to be analyzed, leeches from different sites had to be combined. Thus heavy metal information about some individual sites was lost. However, some sites were not combined. Organisms from different collecting times were never mixed.

Background levels of heavy metals found in the sediments where benthic organisms were taken are not available as a result of a laboratory oversight. However, concentrations of heavy metals present in Lake Superior water are given in Table IV-B-3. For procedures refer to Section V-B-7.

Table IV-B-3 indicates that heavy metals are sequestered by benthic organisms. It appears that the affinity toward different metals varies as they are found at different concentrations. Exceptionally high values of copper and lead were found in organisms collected during July from the dredged channel at C. Reiss Coal Company dock. An analyzed environmental sample from this area might help explain these high levels.

## 4. Discussion

One species of Chrionomidae was successfully reared under laboratory controlled conditions. This organism could be used as an invaluable aid for determining environmental stress. Because of its noted sensitivity to changing rearing conditions, it would be used to determine the precise effects of coal material or other material on the life cycle and physiology. This is the direction that future studies of environmental stress on aquatic organisms should follow.

The kind of species of benthic organisms found in the study area suggest that the water is moderately polluted yet contains low levels of toxic heavy metals (Cairns and Dickson, 1973).

Heavy metals are apparently sequestered by the leech, *Helabdella stagnalis*. This organism is a member of the food chain leading through fish to man. Heavy metals are sequestered by benthic organisms. If these organisms with concentrated levels of toxic material are consumed in large amounts by higher level consumers and the metals further concentrated by top level consumers than there is reason for concern especially if man is the highest level consumer.

Although coal appears not to be harmful to the aquatic system and in fact may be correlated with environmental stability we must not lose sight of the fact that certain metals released either from coal or from other sources are concentrated in organisms at every level in the food chain. Thus low level concentrations of certain materials may be tolerated by organisms occupying a low level in a food chain but these metals may be concentrated through the food chain and may become so toxic in higher level consumers that pathological conditions develop.

22

# 5. Literature Cited

Anderson, E. D. and L. Smith, Jr. 1971. A Synoptic Study of Food Habits of 30 Fish Species from Western Lake Superior. Tech. Bull. 279, Minn. Ag. Expt. Station.

Brown, Harley P. 1972. Aquatic Dryopoid Beetles (*Coleoptera*) of the United States. Environmental Protection Agency, Project No. 18050ELD, Contract No. 14-12-894, 82 pp.

Burch, J. B. 1972. Freshwater Sphaeriacean Clams (Mollusca: Pelecypoda) of Northern America. Environmental Protection Agency, Project No. 18050ELD, Contract No. 14-12-894, 31 pp.

——————— 1973. The Freshwater Molluscs of the Canadian Interior Basin. Malacologia, Vol. 13, 509 pp.

Cairns, J. and K. L. Dickson. 1973. Biological Methods for the Assessment of Water Quality. American Society for Testing and Materials, Philadelphia, Pennsylvania, p. 256.

Eddy, S. and A. C. Hodson. 1961. Toxonomic Keys to the Common Animals of the North Central States. Burgess Publishing Company, Minneapolis, 162 pp.

Edmondson, W. T. 1959. Freshwater Biology. John Wiley and Sons, Inc., New Jersey, 1248 pp.

Holsinger, John R. 1972. The Freshwater Amphipod Crustaceans (*Gammaridae*) of North America. Environmental Protection Agency, Project No. 18050ELD, Contract No. 14-12-894, 89 pp.

Kaill, W. M. and J. K. Frey. 1973. Environments in Profile, an Aquatic Perspective. Canfield Press, pp. 206.

Klemm, Donald J. 1972. Freshwater Leeches (Annelida-Hirudinea) of North America. Environmental Protection Agency, Project No. 18050ELD, Contract No. 14-12-892, 53 pp.

Mason, William T. Jr. 1973. An Introduction to the Identification of Chironomid Larvae. Analytical Quality Control Laboratory National Environmental Research Center, U.S. Environmental Protection Agency, Cincinnati, Ohio, 90 pp.

McCall, Robert B. 1975. Fundamental Statistics for Psychology. Harcourt Brace and Jovanovich, Inc., pp. 406.

Needham, J. G. and P. R. Needham. 1962. A Guide to the Study of Freshwater Biology. Holden-Day, Inc., San Francisco, 108 pp.

Pennak, Robert W. 1953. Fresh-Water Invertebrates of the United States. The Ronald Press Company, New York, 769 pp.

Thomas, W. A., Wilcox, W. H. and G. Goldstein. 1976. Biological Indicators of Environmental Quality. Ann Arbor Science Publishers Inc., Ann Arbor, Michigan, pp. 254.

Williams, W. D. 1972. Freshwater Isopods (*Asellidae*) of North America. Environmental Protection Agency, Project No. 18050ELD, Contract No. 14-12-894, 45 pp.

6mm. culture dish inlet tube

#3 neoprene stopper

air bubble

6" culture dish outlet tube

air valve

air inlet
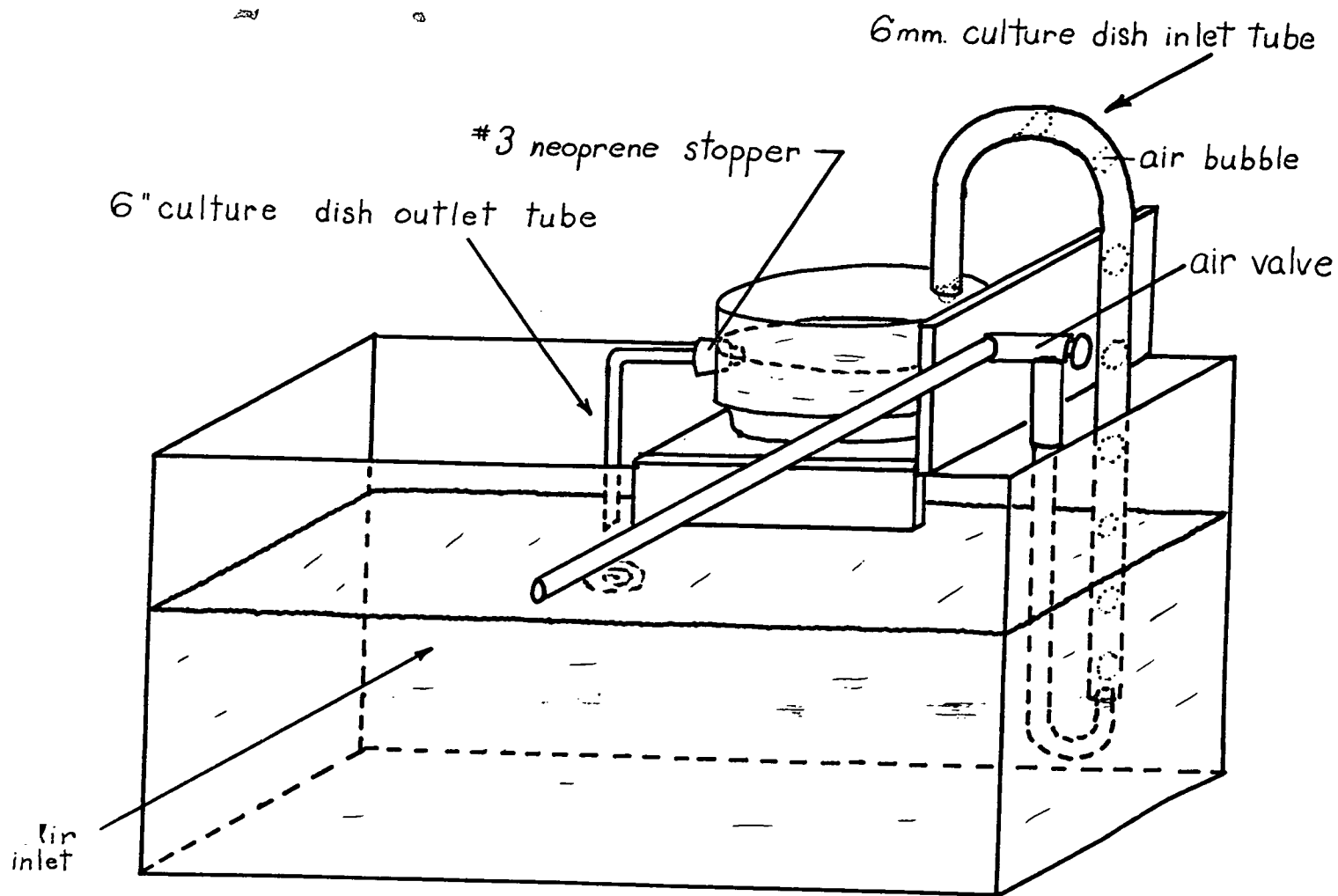
FIG. IV-BI

TABLE IV-B-1

Significance of the Difference in the Diversity Indices

as Related to Seasonal Collecting Times

|  | t Score* |
|---|---|
| Spring Sampling vs. Summer Sampling | 0.009 |
| Summer Sampling vs. Fall Sampling | 0.29 |
| Spring Sampling vs. Fall Sampling | 0.24 |

*Calculated from the equation: $\sigma md = \dfrac{\sigma\ diff.}{\sqrt{n-1}}$

$\sigma md$ = standard error of the mean difference

$\overline{X}$ diff. = mean of the difference data

$\sigma$ diff. = standard deviation of the difference data

McCall, R. B., 1975.

26

TABLE IV-B-2

Correlation and Significance of Site Variations With Sampling Depth

and Between Coal Areas and Non-Coal Areas Using Diversity Indices

| | Coefficient of Correlation* $r_{xy}$ | Significance of the Correlation Coefficient t Value** |
|---|---|---|
| Shallow Site vs. Channel Site | -0.19 | .512 |
| Coal Areas vs. Non-Coal Areas | 0.29 | .802 |

* Values calculated from the equation:

$$r_{xy} = \frac{N\Sigma xy - (\Sigma x)(\Sigma y)}{\sqrt{[N\Sigma x^2 - (\Sigma x)^2][N\Sigma y^2 - (\Sigma y)^2]}}$$

**Values calculated from the equation:

$$t = r_{obs} \frac{\sqrt{N-2}}{\sqrt{1-r_{obs}^2}} \text{ with df = N-2}$$

McCall, R. B. 1975.

TABLE IV-B-3

Concentration of Metal in Organisms (ppm) Dry Weight

| Sample | | As | Ba | Cd | Cr | Co | Cu | Pb | Mn | Mo | Se | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Helobdella stagnalis | | | | | | | | | | | | | |
| M-1 | | 6.7 | 360 | 3.3 | 8.0 | 3.3 | 110 | 22 | 190 | <0.7 | <6.7 | <3.3 | 1270 |
| M-2 | | 5.1 | 70 | 3.1 | 5.1 | 2.3 | 695 | 665 | 275 | <0.3 | <2.6 | <1.3 | 1570 |
| M-3 | | <2.1 | 60 | 2.1 | 1.7 | 1.7 | 45 | 3.4 | 145 | <0.2 | <2.1 | <1.1 | 700 |
| M-4 | | <4.2 | 225 | 0.9 | 4.7 | 1.3 | 45 | 3.5 | 195 | <0.4 | <4.2 | <2.1 | 780 |
| M-5 | | 6.9 | 95 | 1.4 | 5.8 | 2.1 | 140 | 23 | 220 | <0.3 | <3.4 | <1.7 | 400 |
| M-6 | | 3.7 | 129 | 1.1 | 3.3 | 1.9 | 180 | 7.0 | 110 | <0.4 | <3.7 | <1.9 | 140 |
| M-7 | | <1.7 | 75 | 2.2 | 1.0 | 0.8 | 50 | 6.9 | 185 | <0.2 | <1.7 | <0.8 | 400 |
| M-8 | | 2.9 | 135 | 8.7 | 6.7 | 1.4 | 180 | 27 | 145 | <0.3 | <2.9 | <1.4 | 580 |
| M-A-9 | laboratory amphipods | <1.9 | 190 | 0.6 | 1.7 | 0.6 | 40 | 0.8 | 40 | 0.2 | <1.9 | <0.9 | 55 |
| M-I-10 | laboratory isopods | 4.1 | 75 | 2.1 | 2.9 | 1.0 | 265 | 2.9 | 110 | 0.2 | <2.1 | <1.0 | 90 |
| Background concentration of liquid preservation 70% ethyl alchol | | 0.0 | 0.0 | 0.2 | 0.4 | 0.0 | 1.1 | 0.7 | 0.7 | 0.0 | 1.0 | 0.0 | 0.7 |

Concentration of Metal in Lake Water (ppb)

| Sample | As | Ba | Cd | Cr | Co | Cu | Pb | Mn | Mo | Se | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Lake Water | 2 | 37 | 0.6 | 0.3 | 0.9 | 34 | 1.9 | 4.9 | 1.1 | <1 | <1 | 5.5 |

TABLE IV-B-4

Benthic Organisms of the St. Louis River, 9 July 1975

| PHYLA | GENUS | SPECIES | 1-A | 1-B | 1-C | 2-A | 2-B | 2-C | 3-A | 3-B | 3-C |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Nemathelmenthes Nematoda | | | 2 | 1 | | 86 | | 2 | 19 | 17 | |
| Annelida | Marvinmeyer | lucida | | 1 | | | | | | | |
| | Helobdella | elongata | | 3 | 9 | 4 | | 13 | 2 | | 3 |
| | Helobdella | stagnalis | | | 3 | 2 | | 1 | 4 | 8 | 4 |
| | Myzodella | moorei | | | | | 1 | 1 | | | |
| | Illinobdella | alba | | | | | | | | | |
| Mollusca | Sphaerium | transversum | 1 | 1 | | | | | | | |
| | Sphaerium | simile | | | | | | | | | |
| | Sphaerium | lacustre | | 3 | | | | | | | |
| | Sphaerium | nitidum | | | | | | | 22 | | |
| | Sphaerium | securis | 3 | | | 2 | | | | | |
| | Sphaerium | partumium | | | | | | | | | |
| | Sphaerium | rhomboideum | | | | | | | | | |
| | Sphaerium | fabale | | | | | | | | | |
| | Sphaerium | striatinum | | | 1 | | | | | | |
| immature of damaged clams | Sphaerium | occidentale | 1 | | | 3 | 2 | 2 | 1 | 2 | 1 |
| | Promentus | exacuous megas | | | | | | | | | |
| | Gyraulus | deflectus | | | | | | | | | |
| | Helisoma | anceps anceps | | | | | | | | | |
| | Promentus | unbilicatellus | | | | | | | | | |
| | Marstonia | decepta | | | | | | | | | |
| | Amnicola | limnosa | | | 7 | | | | | | |
| | Valvata | sincera | | | 1 | | | | | | |
| | Valvata | tricarinata | | 1 | 3 | | | | | | |
| | Pisidium | fallax | | | | | | | | | |
| immature or damaged snails | | | | | | | | | | | |
| | Eupera | cubensis | 1 | | | | | | | | |
| | Ferrissia | rivularis | | 1 | | | | | | | |
| | Planorbidae | (immature) | | 4 | | | | | | | |
| | Pisidium | dubium | | | | | 1 | | | | |
| | Pisidium | ventrosum | | | | | | | | 1 | |
| | Pisidium | idahoensi | | | | | | | | | |
| | Physa | jennessi | | | | | | | | | |
| DIVERSITY INDICES (D.I.) | | | 4.84 | 3.88 | 4.43 | 1.84 | 1.32 | 3.01 | 3.41 | 2.45 | 2.02 |

TABLE IV-B-4, Continued

Benthic Organisms of the St. Louis River, 9 July 1975

| PHYLA | GENUS | SPECIES | 4-A | 4-B | 4-C | 5-A | 5-B | 5-C | 6-A | 6-B | 6-C |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Nemathelmenthes Nematoda | | | | | | 4 | 13 | 8 | | | |
| Annelida | Marvinmeyer | lucida | | | | | | | | | |
| | Helobdella | elongata | | | | | 1 | 18 | 2 | | |
| | Helobdella | stagnalis | | | | | 1 | 10 | | | |
| | Myzodella | moorei | | | | | | | | | |
| | Illinobdella | alba | | | | | 10 | | | | |
| | Sphaerium | transversum | 6 | 2 | 1 | | | | | | |
| | Sphaerium | simile | | 1 | | | | | 1 | | |
| | Sphaerium | lacustre | | 1 | 6 | | | | 10 | 7 | 2 |
| | Sphaerium | nitidum | | 1 | 1 | | | | | | |
| | Sphaerium | securis | | | | | | | 1 | | 6 |
| | Sphaerium | partumium | | | | | | | | | |
| | Sphaerium | rhomboideum | | | | | | | | | |
| | Sphaerium | fabale | | | | | | | | | |
| | Sphaerium | striatinum | | | | | | | | | |
| | Sphaerium | occidentale | | | | | | | | | |
| immature or damaged clams | | | | | 4 | | 2 | | 4 | 5 | 1 |
| | Promentus | exacuous megas | | | | | | | | | |
| | Gyraulus | deflectus | | | | | | | | | |
| | Helisoma | anceps anceps | | | | | | | | | |
| | Promentus | umbilicatellus | | | | | | | | | |
| | Marstonia | decepta | | | | | | | | 1 | |
| | Amnicola | limnosa | | | | | | | | | |
| | Valvata | sincera | | | | | | | | | |
| | Valvata | tricarinata | | | | | | | | 2 | |
| | Pisidium | fallax | | | | | | | 9 | | 1 |
| immature or damaged snails | | | | | | | | | 1 | | |
| | Eupera | cubensis | | | | | | | | | |
| | Ferrissia | rivularis | | | | | | | 2 | | |
| | Planorbidae | (immature) | | | | | | | | | |
| | Pisidium | dubium | | | | | | | | | |
| | Pisidium | ventrosum | | | | | | | | | |
| | Pisidium | idahoensi | | | | 2 | | | | | |
| | Physa | jennessi | | | | | | | | 1 | |
| DIVERSITY INDICES (D.I.) | | | 1.57 | 2.32 | 2.60 | 1.47 | 3.80 | 4.19 | 5.11 | 5.73 | 4.57 |

30

TABLE IV-B-4, Continued

Benthic Organisms of the St. Louis River, 9 July 1975

| PHYLA | GENUS | SPECIES | 1-A | 1-B | 1-C | 2-A | 2-B | 2-C | 3-A | 3-B | 3-C |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Arthropoda | Gammarus | fasciatus | | | | | | | | | |
| | Gammarus | lacustris | | 1 | 1 | | | | | | |
| | Gammarus | pseudolimnaeus | | 4 | 2 | | | | 1 | | |
| | Hyallella | azteca | | 1 | | | | | | | |
| | Pontoporia | affinis | | | | | | | | | |
| | Asellus | intermedius | | 27 | 6 | | 1 | 3 | | 3 | |
| | Asellus | racovitzai | | | | | | | | | |
| | Rheotanytarsus | sp. | | | | | | | | | |
| | Tribelas | sp. | | | | | | | | | |
| | Cricoptopus | sp. | | | | | | | | | |
| | Lauterborniella | sp. | | | | | | | | | |
| | Procladius | sp. | 3 | | | 23 | 33 | 24 | 34 | 52 | 24 |
| | Parachironomus | sp. | | | 1 | | | | | | |
| | Cryptochironomus | sp. | | | | | 1 | 1 | | 4 | 2 |
| | Chironomus | sp. | | | | | | 1 | | | |
| | Polypedilum | sp. | | | | | | | | | |
| | Coelotanypus | sp. | | | | | | | | | |
| | Potthastia | sp. | | | | | | | | | |
| | Paracladopelma | | | | | | | | | | |
| | Podonominae | sp. | | | | | | | | | |
| Tricoptera | Glossosoma | sp. | | | | | | | | | |
| Tricoptera | Phylocentropus | sp. | | | | | | | | | |
| Tricoptera | Neureclipis | sp. | | | | | | | | | |
| Tricoptera | Molanna | sp. | | | | | | | | | |
| | Leptocella | sp. | | | | | | | | | |
| Insecta | Corixidae Nymph | sp. | | | | | | | | | |
| Insecta | Plecoptera Nymph | sp. | | | | | | | | | |
| | Hexagenia | sp. | | | | | | | | | |
| | Wormaldia | sp. | | | | | | | | | |
| Cladocera | Eurycercus | sp. | | | | | | | | | 1 |
| | Tanypus | sp. | | | | | | | | | |
| | Clinotanypus | sp. | | | | | | | | | |
| | Unidentified | | | | | | | | | | |
| (Crayfish) Astacidae (family) | | | | | | | | | | | |
| Bryozoa | Crystatella | mucedo | | | | | | | | | |

TABLE IV-B-4, Continued

Benthic Organisms of the St. Louis River, 9 July 1975

| PHYLA | GENUS | SPECIES | 4-A | 4-B | 4-C | 5-A | 5-B | 5-C | 6-A | 6-B | 6-C |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Arthropoda | Gammarus | fasciatus | | | | | | | | | |
| | Gammarus | lacustris | | | | | | | | | |
| | Gammarus | pseudolimnaeus | | | | | | | 5 | | |
| | Hyallella | azteca | | | | | | | 1 | 1 | |
| | Pontoporia | affinis | | | | | | | | | |
| | Asellus | intermedius | | | | | 2 | 6 | 28 | | 3 |
| | Asellus | racovitzai | | | | | | | 1 | | |
| | Rheotanytarsus | sp. | | | | | | | | | |
| | Tribelas | sp. | | | | | | | | | |
| | Cricoptopus | sp. | | | | | | | | | |
| | Lauterborniella | sp. | | | | | | | | | |
| | Procladius | sp. | 24 | 15 | 19 | 1 | 5 | 5 | 9 | 5 | 2 |
| | Parachironomus | sp. | | | | | | | | | |
| | Cryptochironomus | sp. | | | | | | | | 2 | 1 |
| | Chironomus | sp. | | | | | | | | | |
| | Polypedilum | sp. | | | | | | | | | |
| | Coelotanypus | sp. | | | | | | | | | |
| | Potthastia | sp. | | | | | | | | | |
| | Paracladopelma | | | | | | | | | | |
| | Podonominae | sp. | | | | | | | | | |
| Tricoptera | Glossosoma | sp. | 1 | | | | | | | | |
| Tricoptera | Phylocentropus | sp. | | 4 | | | | | | | |
| Tricoptera | Neureclipis | sp. | | | | | | | | | |
| Tricoptera | Molanna | sp. | | | | | | | | | |
| | Leptocella | sp. | | | | | | | | | |
| Insecta | Corixidae Nymph | sp. | | | | | | | | | |
| Insecta | Plecoptera Nymph | sp. | | | | | | | | | |
| | Hexagenia | sp. | | | | | | | | | |
| | Wormaldia | sp. | | | | | | | | | |
| Cladocera | Eurycercus | sp. | | | | | | | | | |
| | Tanypus | sp. | | | | | | | | | |
| | Clinotanypus | sp. | | | | | | | 1 | | 3 |
| | Unidentified | | | | | | | | | 1 | |
| (Crayfish) Astacidae (family) | | | | | | | | | | | |
| Bryozoa | Crystatella | mucedo | | | | | | | | | |

32

## TABLE IV-B-5

### Benthic Organisms of the St. Louis River, Summer 1975

| PHYLA | GENUS | SPECIES | 1-A | 1-B | 1-C | 2-A | 2-B | 2-C | 3-A | 3-B | 3-C |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Bryozoa | Grystatella | mucedo | | | | | | | 1 | | |
| Nemathelmenthes Nematoda | | | | | 5 | 29 | 29 | | 8 | | 6 |
| Annelida | Helobdella | elongata | 2 | | 2 | | 1 | | 1 | 5 | 7 |
| | Helobdella | stagnalis | | | 6 | 18 | 5 | | 5 | 5 | 7 |
| Mollusca | Sphaerium | fabale | | | | | | | | | |
| | Sphaerium | lacustre | | | | | | | | 4 | |
| | Sphaerium | partumeium | | | | | | | | 4 | 1 |
| | Sphaerium | securis | | | | | | | | 1 | |
| | Sphaerium | transversum | | | | | | | | | |
| | damaged snails | | | | | 1 | | | | | |
| | Sphaerium | (immature) | | | 3 | 3 | 6 | | | 14 | |
| | Pisidium | fallax | | | | 1 | | | | 2 | |
| | Valvata | tricarinata | 1 | | | | | | | | |
| | Helisoma | anceps anceps | | | | | | | | | |
| | Promentus | exacuous mega | | | | | | | | | |
| | Promentus | umbilicatellus | | | | | | | | | |
| | Amnicola | limnosa | | | | | | | | | |
| | Ferrissia | rivularis | | | | | | | | | |
| | Marstonia | decepta | | | | | | | | | |
| | Gyraulus | deflectus | | | | | | | | | |
| Arthropoda | Asellus | forbesi | | | | | | | | | |
| | Asellus | racovitzai | | | | | | | | | |
| | Asellus | sp. | | | | | 1 | | | | |
| | Asellus | (immature) | 19 | | 2 | | 2 | | | | |
| | Gammarus | fasciatus | | | | | | | | | |
| | Gammarus | lacustris | 5 | | | | | | | | |
| | Gammarus | pseudolimnaeus | | | | | | | | | |
| | Procladius | sp. | | | 5 | 4 | | | 2 | 14 | 1 |
| | Cryptochironomus | sp. | | | | | 2 | | 2 | 1 | |
| | Paracladopelma | | | | | | | | | 3 | |
| | Podonominae | sp. | | | | | | | | | |
| | Coelotanypus | sp. | | | | | | | | | |
| | Glossosoma | | | | | | | | | | |
| | Phylocentropus | sp. | | | | | | | | | |
| | Neureclipsis | sp. | | | | | | | 7 | 3 | |
| | damaged insect | | | | 1 | | | | | | |
| | Polypedilum | sp. | | | | 2 | | | | | |
| **DIVERSITY INDICES (D.I.)** | | | 1.86 | 0.00 | 5.73 | 2.91 | 2.22 | 1.00 | 4.26 | 5.50 | 2.59 |

33

TABLE IV-B-5, Continued

Benthic Organisms of the St. Louis River, Summer 1975

| PHYLA | | GENUS | SPECIES | 4-A | 4-B | 4-C | 5-A | 5-B | 5-C | 6-A | 6-B | 6-C |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Bryozoa | | Grystatella | mucedo | | | | | | | | | |
| Nemathelmenthes Nematoda | | | | | | | 14 | 22 | 13 | | 6 | 1 |
| Annelida | | Helobdella | elongata | | | | 3 | | | 4 | 1 | 1 |
| | | Helobdella | stagnalis | | | | 1 | 1 | 23 | | | |
| Mollusca | | Sphaerium | fabale | 1 | | 2 | | | | | | |
| | | Sphaerium | lacustre | | | | | | | | 1 | 2 |
| | | Sphaerium | partumeium | 1 | | | | | | 2 | | |
| | | Sphaerium | securis | | 2 | 3 | | | | | | |
| | | Sphaerium | transversum | | 1 | 1 | | 1 | | | | |
| | damaged | snails | | | | | | | | 5 | | |
| | | Sphaerium | (immature) | 22 | 2 | 7 | 2 | | | 41 | 5 | 16 |
| | | Pisidium | fallax | | | | | | | 21 | 6 | |
| | | Valvata | tricarinata | | | | | | | 3 | 1 | 1 |
| | | Helisoma | anceps anceps | | | | | | | | 2 | |
| | | Promentus | exacuous mega | | | | | | | 1 | | |
| | | Promentus | umbilicatellus | | | | | | | 1 | | |
| | | Amnicola | limnosa | 2 | | | | | | | | |
| | | Ferrissia | rivularis | | | | | | | 1 | | |
| | | Marstonia | decepta | 3 | | | | | | | | |
| | | Gyraulus | deflectus | | | | | | | 2 | | |
| Arthropoda | | Asellus | forbesi | | | | | | | 66 | | |
| | | Asellus | racovitzai | | | | 1 | | | | | |
| | | Asellus | sp. | | 1 | | | | | | | |
| | | Asellus | (immature) | | | | | | | 16 | | |
| | | Gammarus | fasciatus | | | | | | | 24 | | |
| | | Gammarus | lacustris | | | | | | | 41 | | |
| | | Gammarus | pseudolimnaeus | | | | 1 | | | | | |
| | | Procladius | sp. | 14 | 5 | 14 | | | | 3 | 3 | 3 |
| | | Cryptochironomus | sp. | | 1 | | | 1 | | | | 2 |
| | | Paracladopelma | | | | | | | | | | 1 |
| | | Podonominae | sp. | | | | | | | | 12 | |
| | | Coelotanypus | sp. | | | | | | 1 | | 3 | 1 |
| | | Glossosoma | | 1 | | | | | | | | |
| | | Phylocentropus | sp. | 10 | 5 | | | | | | | |
| | | Neureclipsis | sp. | | | | 1 | 1 | | 7 | | 1 |
| | damaged | insect | | | | | | | | | | |
| | | Polypedilum | sp. | | | | | | | | | |

DIVERSITY INDICES (D.I.)      3.66  4.74  3.02  2.48  1.28  1.99  6.22  6.02  3.01

## TABLE IV-B-6

## Benthic Organisms of the St. Louis River, Fall 1975

| PHYLA | GENUS | SPECIES | 1-A | 1-B | 1-C | 2-A | 2-B | 2-C | 3-A | 3-B | 3-C |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Platyhelminthes | | | | | | | | | | | |
| Turbellaria (class) | | | | | | | | | | | |
| Bryozoa | Crystatella | statoblast | | | | | 1 | | | | |
| Annelida | Helobdella | stagnalis | 1 | 2 | | 2 | 4 | | | | |
| | Helobdella | elongata | | | | 10 | 8 | | | | 2 |
| | unidentified but large unique sp. | | | | | | | | | | |
| | Valvata | tricarinata | | | | | | | | | |
| | Glossiphonia | complanata | | | | | | | | | |
| Mollusca | Sphaerium | simile | 1 | | | | | | | | |
| | Sphaerium | sp. | | 2 | | | 1 | | | | |
| | Sphaerium | striatinum | | | 1 | | | | | | |
| | Sphaerium | securis | | | | 3 | | | | | |
| | Sphaerium | fabale | | | | | | | | | |
| | Sphaerium | transversum | | | | | | | | | |
| | Sphaerium | occidentale | | | | | | | | | |
| | Sphaerium | lacustre | | | | | | | | | |
| | Sphaerium | partumeium | | | | | | | | | |
| | Sphaerium | (immature) | | | | | | | | | |
| | Valvata | tricarinata | 1 | | | | | | | | |
| | Amnicola | limnosa | | 2 | | | | | | | |
| | Ferrissia | rivularis | | 5 | | | | | | | |
| | Pisidium | fallax | | | | | | | | | |
| | damaged snails | | | | 1 | | | | | | |
| Arthropoda | Chironomus | sp. | 1 | 19 | | | | | | | |
| | Asellus | racovitzai | 7 | | | | | | | | |
| | Asellus | sp. (immature) | | 100 | 12 | | | | | | |
| | Asellus | sp. | | | | | | | | 1 | |
| | Glyptotendipes | | | 5 | | | | | | | |
| | Gammarus | fasciatus | | 19 | | | | | | | |
| | Gammarus | lacustris | | | 5 | | | | | | |
| | Gammarus | pseudolimnaeus | | | | | | | | | |
| | Procladius | sp. | | | | 5 | 4 | | 3 | 7 | 8 |

35

TABLE IV-B-6, Continued

Benthic Organisms of the St. Louis River, Fall 1975

| PHYLA | GENUS | SPECIES | 4-A | 4-B | 4-C | 5-A | 5-B | 5-C | 6-A | 6-B | 6-C |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Platyhelminthes | | | | | | | | | | | |
| Turbellaria (class) | | | | | | | | | 5 | | |
| Bryozoa | Crystatella | statoblast | | | | | | | | | |
| Annelida | Helobdella | stagnalis | | | | 3 | | 20 | | | 2 |
| | Helobdella | elongata | | | | 2 | | 4 | | | |
| | unidentified but large | unique sp. | | | | | | 1 | | | |
| | Valvata | tricarinata | | | | | | | | 1 | 1 |
| | Glossiphonia | complanata | | | | | | | | | |
| Mollusca | Sphaerium | simile | | | | | 1 | | | | |
| | Sphaerium | sp. | | | | | | | | | |
| | Sphaerium | striatinum | | | | | 1 | | | | |
| | Sphaerium | securis | | | | | | | | | |
| | Sphaerium | fabale | 4 | | | | | | | | |
| | Sphaerium | transversum | 1 | | | | | | | | |
| | Sphaerium | occidentale | 1 | | | | | | | | |
| | Sphaerium | lacustre | | | | | | 1 | | 1 | |
| | Sphaerium | partumeium | | | | | | | | | 1 |
| | Sphaerium | (immature) | 7 | | | | | | | 2 | 9 |
| | Valvata | tricarinata | | | | | | | | | |
| | Amnicola | limnosa | | | | | | | | | |
| | Ferrissia | rivularis | | | | | | | | | 1 |
| | Pisidium | fallax | | | | | | | | 1 | 1 |
| | damaged snails | | | | | | | | | | 1 |
| Arthropoda | Chrionomus | sp. | | | | | | | | | 17 |
| | Asellus | racovitzai | | | | 1 | | 5 | | | 21 |
| | Asellus | sp. (immature) | 2 | 3 | 1 | | | | | | 42 |
| | Asellus | sp. | | | | | | | | | |
| | Glyptotendipes | | | | | | | | | | 1 |
| | Gammarus | fasciatus | | | | 6 | | | | | 5 |
| | Gammarus | lacustris | | | | | | | | | 5 |
| | Gammarus | pseudolimnaeus | | | | | | | | | 4 |
| | Procladius | sp. | | | | 2 | | 4 | | 5 | 14 |

36

TABLE IV-B-6, Continued

Benthic Organisms of the St. Louis River, Fall 1975

| PHYLA | GENUS | SPECIES | 1-A | 1-B | 1-C | 2-A | 2-B | 2-C | 3-A | 3-B | 3-C |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Arthropoda (continued) | Cryptochironomus | | | | | 1 | | | 1 | 1 | |
| | Potthastia | longimanus | | | | | | | | | |
| | Microtendipes | | | | | | | | | | |
| | Dicrotendipes | nervoses | | | | | | | | | |
| | Coelotanypus | sp. | | | | | | | | | |
| | Einfeldia | sp. | | | | | | | | | |
| | Hyalella | azteca | | | | | | | | | |
| Astacidae (family) | | | | 1 | | | | | | | |
| Insecta (class) | | | | | | | | | | | |
| Trichoptera (order) | Neureclipsis | sp. | 13 | 1 | 3 | | | | 1 | 3 | 2 |
| Insecta (class) | | | | | | | | | | | |
| Plecoptera (order) | Isoperia | sp. | | | | | | | | | |
| Nemathelmenthes Nematoda | | | | | | | | | | | |
| | | | | | | | | | | | |
| DIVERSITY INDICES (D.I.) | | | 2.59 | 2.29 | 2.46 | 3.17 | 3.02 | 1.00 | 3.52 | 2.20 | 3.00 |

37

TABLE IV-B-6, Continued

Benthic Organisms of the St. Louis River, Fall 1975

| PHYLA | GENUS | SPECIES | 4-A | 4-B | 4-C | 5-A | 5-B | 5-C | 6-A | 6-B | 6-C |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Arthropoda (continued) | Cryptochironomus | | | | | | | 1 | | 3 | 5 |
| | Potthastia | longimanus | | | | | | 2 | | 1 | |
| | Microtendipes | | | | | | | | | 1 | |
| | Dicrotendipes | nurvoses | | | | | | | | 1 | |
| | Coelotenypus | sp. | | | | | | | | 1 | 6 |
| | Einfeldia | sp. | | | | | | | | | 1 |
| | Hyalella | azteca | | | | | | | | | 5 |
| Astacidae (family) | | | | | | 1 | | | | | |
| Insecta (class) | | | | | | | | | | | |
| Trichoptera (order) | Neureclipsis | sp. | | | | 2 | | | | | |
| Insecta (class) | | | | | | | | | | | |
| Plecoptera (order) | Isoperia | sp. | | | | | | | | 2 | |
| Nemathelmenthes Nematoda | | | | | 1 | 2 | | 13 | | | 1 |
| DIVERSITY INDICES (D.I.) | | | 3.17 | 1.00 | 3.60 | 4.09 | 2.00 | 4.11 | 1.00 | 7.37 | 6.97 |

38

# V. CHEMICAL RESEARCH

## A. BASIC EXPERIMENTAL DESIGN

The major thrust of the chemistry portion of this study was to determine the factors which were instrumental in mobilizing environmentally hazardous materials (heavy metal ions) from the static coal storage piles.[8] In the consideration of factors which could be effective in mobilization of heavy metals from the coal, and allowing their subsequent release to the aquatic environment of the Duluth-Superior Harbor, the primary mode of mobilization was assumed to be that of water. This water was found to be primarily of three sources:

1. rain falling on the coal and its subsequent leaching through the pile
2. snow falling on the coal, eventually melting and then leaching through
3. water drawn from the bay, and sprayed on the coal as a dust abatement procedure

Therefore, additional parameters were deemed necessary to provide the needed experimental control of the water leachant. These parameters were chosen to provide the maximum amount of information as to the effects of aqueous leaching on the static coal pile. The following additional parameters were:

1. pH control: The solubility of many metal ions is dependent on the hydrogen ion concentration of the medium in contact with the ions. Elements such as arsenic or chromium which occur as oxyanions, could be expected to mobilize under different conditions from other elements such as copper, or cobalt, which would occur as cationic species. In addition, if many of the metals were bound by anionic sites on the coal, the pH of the leachant could have a profound effect on solubility and mobilization. Also, since the western coal is low in sulfur content and relatively high in alkaline earths, it tends to give an alkaline leachant.

2. Rate of percolation through the coal (leachant-coal contact): It was necessary to control the rate of percolation through the coal to investigate the effect of contact between the coal and leachant. The concentration of metal ions in the leachate could be influenced by the amount of additional material removed from the coal, due to an "equilibrium" set-up between the leachate and the coal.

Other factors were determined to have probable effects on heavy metals leaching from the coal. These factors were chosen to explore the influence of temperature, oxidizing versus non-oxidizing atmosphere, and size of the coal particles. The rationale for the choice of the above factors may be summarized in the following manner:

39

1. Since there are wide temperature ranges to be found in the storage area for the coal (air temperature above 90°F in summer and below -30°F in the winter), the effects of changes in the temperature of the leachant on the mobilization of heavy metals was necessary. Also, it was necessary to determine the effects of elevated temperature, since spontaneous interior heating of the coal pile occurred.

2. Conditions on and in the coal storage pile were found to range from oxidizing at the surface (exposure to air, heat, light) to non-oxidizing in the interior of the pile (removal of oxygen by reaction with the coal). It was considered to be extremely important to determine whether the solubilization and mobilization of the heavy metals occurred more readily under oxidizing or non-oxidizing conditions.

3. It had been noted that the western coal was of a "soft" character, and relatively porous in nature. Thus it was necessary to determine if the removal of the heavy metals from the coal by an aqueous leachant was a function of the surface area of the coal in contact with the leachant, or whether the coal was permeable to a sufficient extent to render the particle size of the coal of no consequence.

As a result of the above considerations, the following factors were set as the parameters to be controlled in the first major leaching study:
1. temperature
2. gas saturation of leachant ($N_2$ or $O_2$ atmosphere)
3. rate of leachant flow
4. particle size of coal
5. pH of leachant

The above listed parameters were the factors chosen, and were the first to be investigated. As the coal study progressed, additional avenues of investigation presented themselves and were made the subject of research.


B. EXPERIMENTAL DESIGN AND DESCRIPTION OF SUPPORTING EQUIPMENT AND SUPPLIES

1. Coal Samples

The leaching study was carried out in three different samples of coal.

Western Coal No. 1[6]--
This sample was obtained from one of the cars of a unit train which was transporting the coal from the western mines to the coal transshipment facility in Superior, Wisconsin. The coal car was selectively sampled, and all portions were combined and stored (as a single composite sample) in a polyethylene bag.

Western Coal No. 2[6]--
This sample was obtained from the coal pile at the Superior transshipment facility. A bulldozer was used to dig down approximately two meters into the coal pile, so that a sample which had not been exposed for a long period of time to the effects of air, or air-borne contaminants, could be obtained. The sample was collected and stored in a polyethylene bag until

processed for experimentation.

Eastern Coal[4]--

The sample of eastern coal was furnished to the CLSES research group through the assistance of the Detroit Edison Company, who sampled their stockpile at the Detroit power plant. The sample was shipped to the local laboratory in a polyethylene lined container.

## 2. Coal Grinding

It should be noted that all coal samples were quite moist when obtained. The polyethylene bags were kept sealed, and the high amount of moisture became apparent as a condensate on the inner surface of the sample bags. It was necessary to air-dry portions of the samples for at least 24 hours before grinding and sieving operations could be performed, otherwise the damp coal "gummed up" both the mill and the stainless steel sieves to the point that accurately sized fractions could not be obtained.

The coal, as obtained from the various sources of supply, ranged from fine dust up to lumps approximately five cm (two inches) across the largest dimension.

A Thomas-Wiley® Laboratory Mill-Model 4 was used in the grinding process. The knives (both stationary and moving) were adjusted according to the specified tolerances recommended by the manufacturer. A 2 mm exit screen was used to set the maximum size for the ground coal. A single pass of the coal through the mill was sufficient to reduce the coal to the desired ranges of particle sizes. Further passes through the mill did not significantly reduce the sizes of the larger particles or increase the amount of "fines."

## 3. Stainless Steel Sieves

On examination of available sieves of standard mesh sizes, it was noted that the usual sieve was fabricated from the brass wire cloth soldered to a brass frame. Construction of this nature was deemed unacceptable due to possible contamination of the samples with heavy metals (copper, zinc, lead) by abrasion of the screen or wall material during the sieving process.

It was found that the same type of sieve was available with stainless steel construction throughout. Specimens of these sieves were obtained and were found to be unacceptable since the stainless steel sieve cloths were mounted to the rims by the use of a soft solder which could be abraded by the sieving process and contaminate the sample.

Upon consultation with the fabricator, S.W. Tyler Co., it was found to be possible to fabricate solder-free sieves of all stainless steel construction, and the company prepared a set of screen to those specifications.

## 4. Sieving Technique

The ground coal sample obtained by passage of the crude coal sample through a Wiley® Mill, was placed in a stainless steel sieve stack consist-

ing of 2 mm, 1 mm, 0.5 mm, 0.25 mm, 0.125 mm and 0.063 mm sieves. The stacked sieves were covered with a stainless steel cover and a stainless steel pan to collect the "fines" was placed on the bottom of the stacked sieves.

The sieve stack was placed in a Ro-Tap® apparatus and the sample was shaken with tapping for approximately 15 minutes. At the end of the shaking period, the stacked sieves were separated, and the various fractions were brushed from the sieves into polyethylene containers, using a plastic-bristle brush. The containers were closed with polyethylene lids and the sized coal samples were stored until needed.

## 5. Deionized Water

Deionized water from the experimental work performed in this study was prepared through the use of a Millipore® system consisting of the following components and sequence.

Water from the city mains was drawn into the purification train through a plastic tube, then through a Milli-Q3® unit (prefiltration and reverse osmosis) and finally through a Milli-Q2® system of cartridges containing activated carbon and ion exchange resins. This treatment produced purified, deionized water from sufficient purity to give zero readings for the metals being determined by flameless atomic absorption spectrophotometric analysis.

## 6. Continuous Flow Leaching Apparatus

This apparatus was used in the coal leaching studies which involved continuous flow of the leachant through the coal. Since the same system was used in all recirculating (continuous flow) studies, a single description of the apparatus will suffice. See Figures V-B-1 through V-B-3 for details of construction.

The leaching apparatus was fabricated entirely from polypropylene bottles and tubing, polypropylene fittings and tubing connectors, polytetrafluoroethylene (Teflon®) screening and flexible silicone rubber tubing. Thus, the leaching fluid, as it circulated, came only in contact with coal and/or plastic. In this manner, trace metal contamination from outside sources was minimized, and the concentrations of metal ions in the leachate may be assumed to be derived from the coal in contact with the circulating leachant.

The principal leaching study module consisted of a nominal 2-liter (one-half gallon) polypropylene bottle with a polypropylene screw cap. The bottle cap was fitted with four polypropylene tubes which served as leachant inlet, leachant outlet, gas inlet and gas outlet--volume makeup, respectively. The polypropylene tubes were passed through the bottle cap by means of polypropylene bulkhead fittings.

The leachate outlet tube was fitted with a polypropylene thistle-tube top, to which was attached at 74-micron Teflon® screen. The fluoropolymer screen was mounted on the thistle-tube top my means of a polypropylene fiber which was used to tie the screen across the opening. The function of the Teflon® screen was to minimize the passage of fine particles of coal through

the tubing and tubing pump, so that only solubilized materials were recirculated through the system.

Polypropylene tubing (one-quarter inch size) lines were used to conduct the leachant solution to and from the tubing roller pump heads. All changes in direction of the polyolefin tubing were made with ninety degree (90°) elbow fittings which were fabricated from polypropylene. Unit fittings were used to attach a length of flexible silicone rubber tubing to the inlet and outlet polypropylene lines. The flexible silicone tubing was necessary to give the necessary pumping action through the roller pump heads of the tubing pump.

A change of ground and properly sized coal was placed in the bottom of the leaching bottle. The amount of coal was such that the bottle was approximately one-quarter to one-third full of coal. Sufficient leaching solution (leachant) was then added to completely cover the coal and have the bottle approximately two-thirds full with the coal-leachant mixture. The volume of leachant used was in the range of 800-1000 ml.

Leachant was drawn from the center fo the leaching bottle, and as near the bottom of the bottle as was possible. This placement of the outlet tube was to allow the maximum percolation of the leaching fluid through the pulverized coal-bed in the bottle. The leachant inlet tube was terminated above the surface of the liquid in the leaching bottle, so that the continuous cycle of fluid was broken. This termination was done for a two-fold purpose. The passage of the return flow of the leachate through the gas space above the leachant-coal served to keep the leachant saturated with the gas used as atmosphere in the particular run, and in addition, the impact of the returning leachant stream acted as a partial stirring aid in order to facilitate mixing of the leachate and to minimize channeling effects through the coal-bed.

The leachate inlet tube, on its return from the tubing pumphead, was split and a "T-joint" inserted. A dust-protected tube was attached to the "T-joint" and served as the sample withdrawal point. Sample makeup volume was returned to the system through the gas outlet tube in the bottle cap.

Flexible silicone rubber tubing was used to conduct the cylinder gases (which maintained the controlled gas space over the coal) from the storage cylinders to the gas washing train. The individual parts of the gas washing train were also connected by silicone tubing.

Commercial cylinder gases (nitrogen and oxygen) were purified through a sealed, seven-bottle washing train. The gases passed serially from the tank through (1) a ballast bottle, (2) 6 N sulfuric acid, (3) 6 N sulfuric acid, (4) deionized water, (5) 6 N sodium hydroxide, (6) deionized water, and (7) deionized water. With the exception of the initial ballast bottle and surge tank which was of glass, the remaining six bottles of the train were polypropylene. The gas train was pressurized to approximately 10 psig to give adequate control of gas flow to each leaching module through a gas splitting manifold. The long distance run (approximately 2 meters) from the gas washing train to the gas splitting manifold was polypropylene tubing. The gas

splitting manifold was polypropylene valves and tubing. The final connections to the leaching bottles was silicone rubber tubing.

The total continuous flow leaching system consisted of a 300 liter (80 gallon) rectangular constant temperature bath which was fitted with temperature controllers (thermostats, heaters and cooling coils) and stirrers. A total of six leaching bottles, fitted with leachant circulating lines and gas feeds (for controlled atmosphere) could be accommodated in the constant temperature tank at one time. Thus, four runs and two "control" bottles could be carried out as a simultaneous process.

## 7. Chemical Analysis of Biological Samples

Oven-dried samples of vascular macrophytes and benthic organisms (as provided by the biological research groups) were prepared for metal analysis by the following procedure.

Samples, in the size range of 0.08-0.10 g, were accurately weighed on an analytical balance. The weighed samples were then placed in Parr ® Teflon ® lined acid digestion bombs and 2.50 to 3.00 ml of ultrapure, concentrated nitric acid were added.[12] The acid digestion bombs were then assembled, sealed and heated in an oven at 150°C for a period of two to three hours.

The digestion bombs were removed from the oven and allowed to cool to room temperature. The bombs were then opened and the contents were quantitatively transferred to volumetric flasks and diluted to a standard volume with deionized water.

Samples, after digestion, were analyzed for metal content by the use of flameless atomic absorption spectrophotometry.[1, 2, 10, 11, 15, 16]

44

# BOTTLE CAP SCHEMATIC
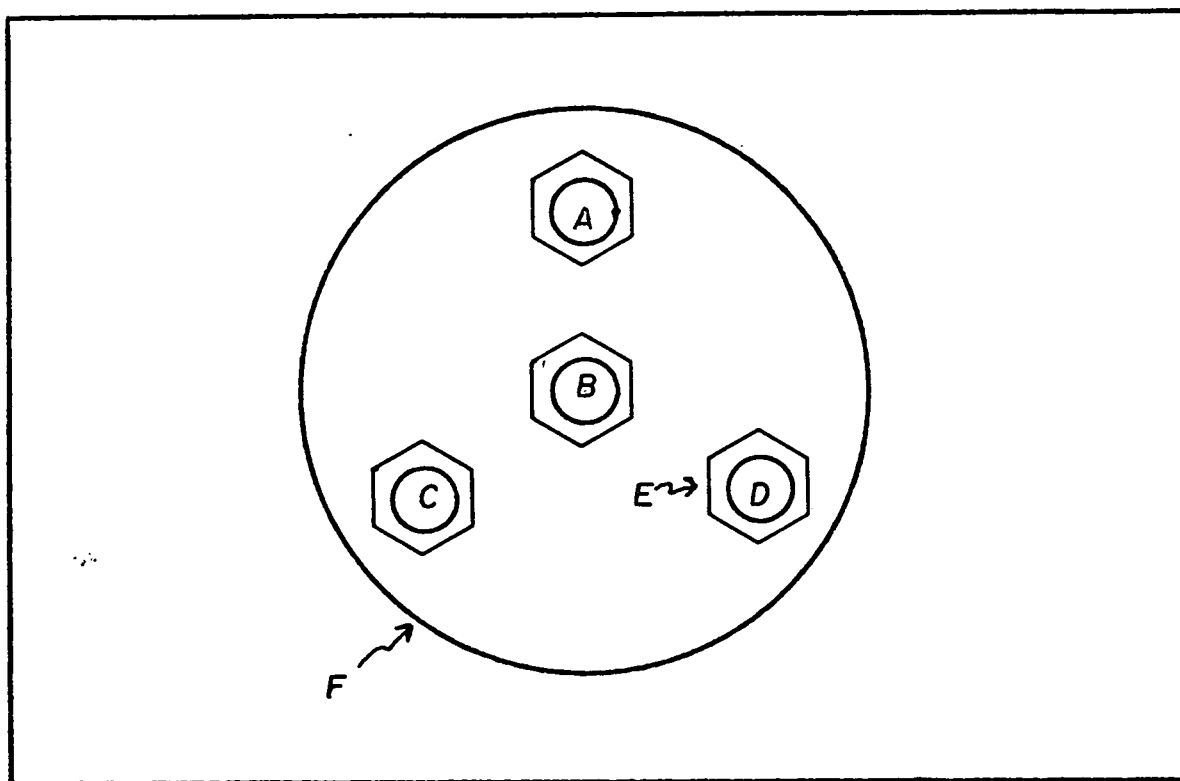


FIGURE V-B-1

LEGEND FOR FIGURES V-B-1 AND V-B-2

A.  LEACHATE INLET TUBE

B.  LEACHATE OUTLET TUBE

C.  GAS INLET TUBE

D.  GAS OUTLET AND LIQUID VOLUME MAKEUP TUBE

E.  BULKHEAD FITTING

F.  BOTTLE CAP

G.  2-LITER LEACHING BOTTLE

H.  THISTLE TUBE END

I.  74-MICRON TEFLON SCREEN

NOTE:  ALL PARTS OF SYSTEM ARE POLYOLEFIN PLASTIC OR TEFLON.
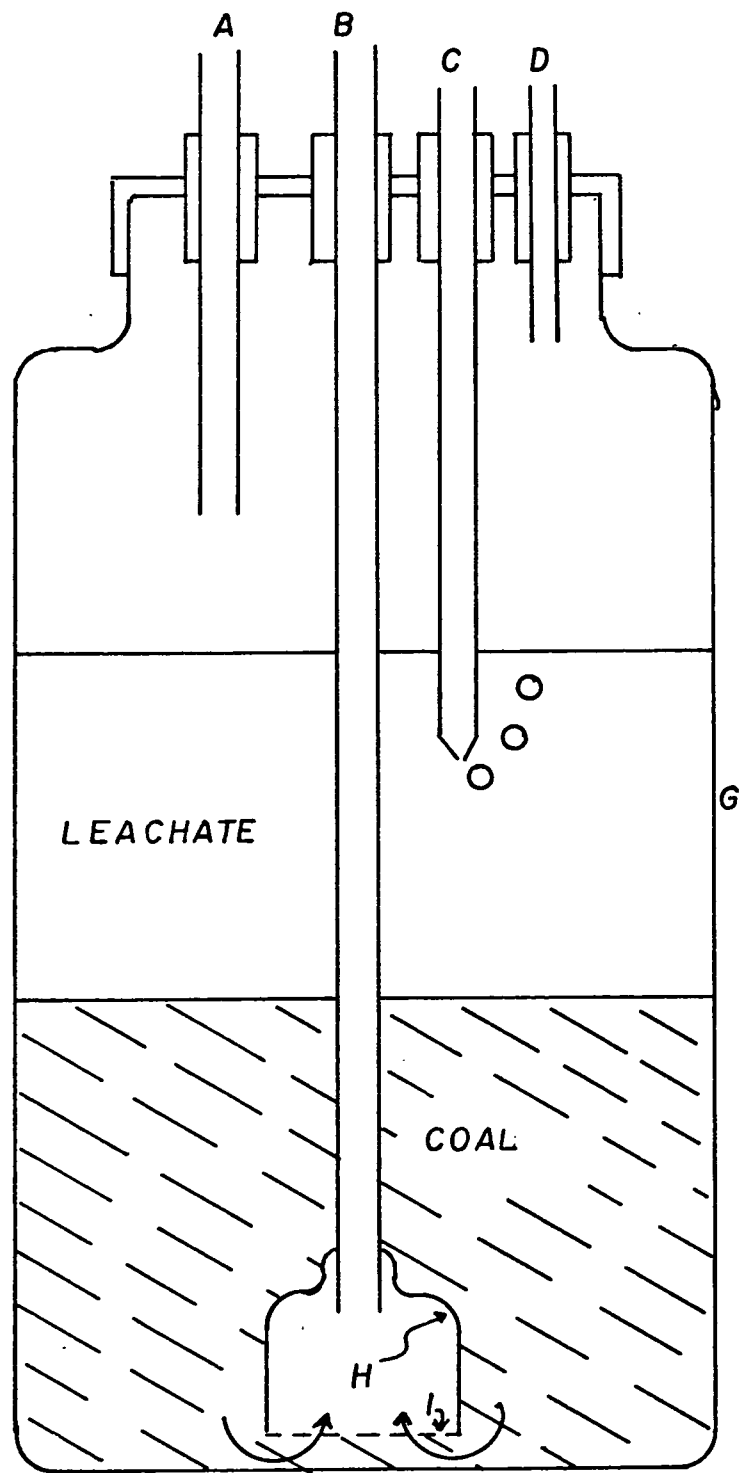
FIGURE V-B-2

# CONTINUOUS FLOW LEACHING SYSTEM

## C. EXPLORATORY EXPERIMENTS

### 1. Coal Titration

#### a. Experimental--
This experiment was formulated to give an approximate "equivalent weight" of the coal in terms of its ability to react with either acid or base.

Separate 2.00 gram samples of coal (Western Coal No. 1) were placed in pre-rinsed polyolefin bottles and covered with forty millimeters of deionized water. Particle sizes of coal used in the separate samples were:
1. 0.500 - 1.00 mm
2. 0.250 - 0.500 mm
3. 0.125 - 0.250 mm
4. 0.063 - 0.125 mm

Successive five ml portions of standard acid or base were added to each sample every 24 hours. The sample was then agitated and allowed to stand for a period of 24 hours, after which time, the pH of the system was measured with a pH meter.

The pH of each particle size of coal was then plotted versus milliliters of titrant added (see Fig. V-C-1).

#### b. Results and Discussion--
A plot of pH versus ml of acid or base is shown in Fig. V-C-1. The curve appears as a typical, multi-functional, weak acid or weak base titration curve. There is some effect due to particle size, with larger particle sizes showing a smaller buffer effect, only at higher pH value.

The buffer effect appears to be more of a bulk effect rather than a surface effect. With 35 ml of base added, the pH was about 9.5 for the largest particles and about 8.5 for the smallest particles. If there was no coal present, the pH should have been 11.7. Calculation will show that the 2.00 g of coal reacted with $2.1 \times 10^{-3}$ m moles of $OH^-$ ion for the large particles and $4.2 \times 10^{-3}$ m moles of $OH^-$ ion for the small particles. This is a 2 to 1 ratio. Assuming spherical particles and constant density, gives the small particles 8 times the surface area of the large particle. Also, the curves show the 35 ml, base addition point as about the largest surface effect obtained. It would seem, therefore, that the reaction of the coal with acid or base is primarily a bulk effect.

The actual runs using an acetic acid-sodium acetate buffer gave 0.142 m mole $H^+$ per gram of coal to reach a pH of 4.85. A similar calculation using the data from this experiment gave a value of 0.170 m mole $H^+$ per gram of coal to reach pH = 4.85. The two values are in reasonably good agreement and an average value of 0.16 m mole $H^+$ per gram of coal to reach pH = 4.85 seems to be fairly reliable.

Using 0.16 m mole $H^+$ per gram of coal yields a value of 150 equivalents of $H^+$ to bring 1 ton of coal to pH = 4.85. This would be equivalent to about 4.0 liters of concentrated sulfuric acid per 1 ton of coal, or in pure metric

## C. EXPLORATORY EXPERIMENTS

### 1. Coal Titration

a. Experimental--

This experiment was formulated to give an approximate "equivalent weight" of the coal in terms of its ability to react with either acid or base.

Separate 2.00 gram samples of coal (Western Coal No. 1) were placed in pre-rinsed polyolefin bottles and covered with forty millimeters of deionized water. Particle sizes of coal used in the separate samples were:
1. 0.500 - 1.00 mm
2. 0.250 - 0.500 mm
3. 0.125 - 0.250 mm
4. 0.063 - 0.125 mm

Successive five ml portions of standard acid or base were added to each sample every 24 hours. The sample was then agitated and allowed to stand for a period of 24 hours, after which time, the pH of the system was measured with a pH meter.

The pH of each particle size of coal was then plotted versus milliliters of titrant added (see Fig. V-C-1).

b. Results and Discussion--

A plot of pH versus ml of acid or base is shown in Fig. V-C-1. The curve appears as a typical, multi-functional, weak acid or weak base titration curve. There is some effect due to particle size, with larger particle sizes showing a smaller buffer effect, only at higher pH value.

The buffer effect appears to be more of a bulk effect rather than a surface effect. With 35 ml of base added, the pH was about 9.5 for the largest particles and about 8.5 for the smallest particles. If there was no coal present, the pH should have been 11.7. Calculation will show that the 2.00 g of coal reacted with $2.1 \times 10^{-3}$ m moles of OH$^-$ ion for the large particles and $4.2 \times 10^{-3}$ m moles of OH$^-$ ion for the small particles. This is a 2 to 1 ratio. Assuming spherical particles and constant density, gives the small particles 8 times the surface area of the large particle. Also, the curves show the 35 ml, base addition point as about the largest surface effect obtained. It would seem, therefore, that the reaction of the coal with acid or base is primarily a bulk effect.

The actual runs using an acetic acid-sodium acetate buffer gave 0.142 m mole H$^+$ per gram of coal to reach a pH of 4.85. A similar calculation using the data from this experiment gave a value of 0.170 m mole H$^+$ per gram of coal to reach pH = 4.85. The two values are in reasonably good agreement and an average value of 0.16 m mole H$^+$ per gram of coal to reach pH = 4.85 seems to be fairly reliable.

Using 0.16 m mole H$^+$ per gram of coal yields a value of 150 equivalents of H$^+$ to bring 1 ton of coal to pH = 4.85. This would be equivalent to about 4.0 liters of concentrated sulfuric acid per 1 ton of coal, or in pure metric

units, 4.4 liters of concentrated sulfuric acid per metric ton of coal.

## 2. Design of Buffer System for Low pH Runs

Western Coal produced slightly alkaline solutions in distilled water, and it was suspected that the buffer capacity of the coal was appreciable. In order to make leaching runs at pH values other than the natural buffer point of the coal, it became necessary to design buffer solutions.

Attempts were made to design:
1. an alkaline buffer near pH = 10 using $CO_3^{2-}$, $HCO_3^-$ system
2. an acid buffer near pH = 5 and pH = 6 using a $HCO_3^-$, $H_2CO_3$ system
3. an acid buffer near pH = 5 using a $C_2H_3O_2^-$, $HC_2H_3O_2$ system

Of the three systems, only system 3 was usable. The basic (near pH = 10) system gave leachates which were very concentrated in interferring materials (probably organic). These leachates actually blackened the quartz windows of the atomic absorption furnace and were thus impossible to analyze using the methods adopted for this work. The $HCO_3^-$, $H_2CO_3$ system would not hold pH due to escape of $CO_2$ to the atmosphere.

The final buffer of choice was 0.072 M $HC_2H_3O_2$ and 0.028 M ($Na^+$, $C_2H_3O_2^-$) in deionized water. Runs with this leachant are designated as "acetate buffer" runs. This system:
1. gave no background heavy metal contamination
2. gave no significant interferences in the atomic absorption analyses
3. held the pH of the system at 4.85 plus or minus a few tenths of a pH unit during the leaching runs. Final pH values for the first factorial run gave $\sigma = 0.024$ pH units.

Assuming a pH of 4.74 for $HC_2H_3O_2$ gives an initial pH of 4.33 for the buffer. Using 1,000 ml of original leachate applied to 200 g of coal and a final pH of 4.85 as data, routine calculations show that 28.3 m moles of $HC_2H_3O_2$ are neutralized by 200 g of coal. This yields 0.142 m moles $H^+$ used per gram of coal to reach a pH of 4.85.

In comparison, the HCl titration of coal gives 0.170 m moles $H^+$ used per gram of coal to reach pH = 4.85.

## 3. Filter Uptake Study

It was suspected that lead ion was adsorbed on Millipore® filters and thus lost to the analysis. A series of experiments, here reported, seem to show that the effect is real.

Samples of both deionized water and Lake Superior water were spiked with lead ion and the loss on filtering through 0.45μ Millipore® filters was measured with the atomic absorption spectrophotometer. On the deionized water samples, filtration time was ∿3 min. Filtration time for the lake water runs was ∿2 min. Results are shown in Figures V-C-2 and V-C-3. One set of the filters from the deionized water runs were washed with 0.01 N CHl (ultra-pure) and another set of the filters were washed with a 1.0 ppm $Al^{3+}$ ion

solution (lead free). Lead was measured in these filtrates and the results combined with the original filtrates to give total lead recovery with wash (see Fig. V-C-4). These results imply that, at least at the higher concentrations of lead ion, significant amounts of lead are retained on the filters. Even though an acid or Lewis acid wash can recover this lead, the nature of the coal leaching system may not allow an acid wash or pretreatment of the sample before filtration.

It should be noted that, at the 10 ppb level, there was considerably less loss of lead from the lake water sample than from the deionized water sample. This protection of the lead ion, possibly by complexation, should be considerably enhanced in media such as coal leachates and bottom lake samples. Nevertheless this filter adsorption is of serious concern in any lead analysis of filtered water samples.

At this point in the research, it was decided (by definition) that a metal was mobilized by the leachant if the metal passed a 0.45μ filter (a fairly standardized particle in this type of work). Any acid treatment of the leachate prior to filtration or acid wash of the filter would have disturbed the system by changing the properties of residual colloids and other particles in the system.

In this work, no lead was observed to leach from the coal with pure water, however, these results must be held inconclusive at this time.

A future, detailed study of filter absorption from coal leachate would certainly be in order.

## 4. Extremum Runs

Preliminary to the large experimental designs, some coal was subjected to the extreme conditions that might be expected in the coal handling facility.

a. Experimental --
   Three samples of coal grindings were subjected to extreme conditions:
(1) One sample (50% coal - 50% water by weight was shaken on a fast shaker at room temperature for 72 hours. The mud obtained was unfilterable. No analysis was done.
(2) One sample (50% coal - 50% water) was subjected to alternate freezing and thawing for 1 week under still (not shaken) conditions. Analytical results were Cu-4.0 ppb; Mn-2.1 ppb; Ba-70 ppb. V and Mo were below detection limits.
(3) One sample (50% coal - 50% water) was held near 100°C in a steam bath for 6 days. Analytical results were Cu-10.7 ppb; Mn-6.8 ppb; Ba-160 ppb. V and Mo were below detection limits.

b. Discussion --
   Experiment (1) shows that the coal is rather fragile. As no analysis was done, no further conclusions were drawn.

Experiments (2) and (3) do show a 2 to 3 fold increase in metal extraction for sub-boiling conditions over the extractions obtained for freeze-thaw conditions.

The temperature effect was studied in some detail in the later work. The interesting point, however, is that alternate freezing and thawing did not release large amounts of metal ions. Because many open storage piles will be subjected to moist, freeze-thaw cycles, this fact is certainly of environmental significance.
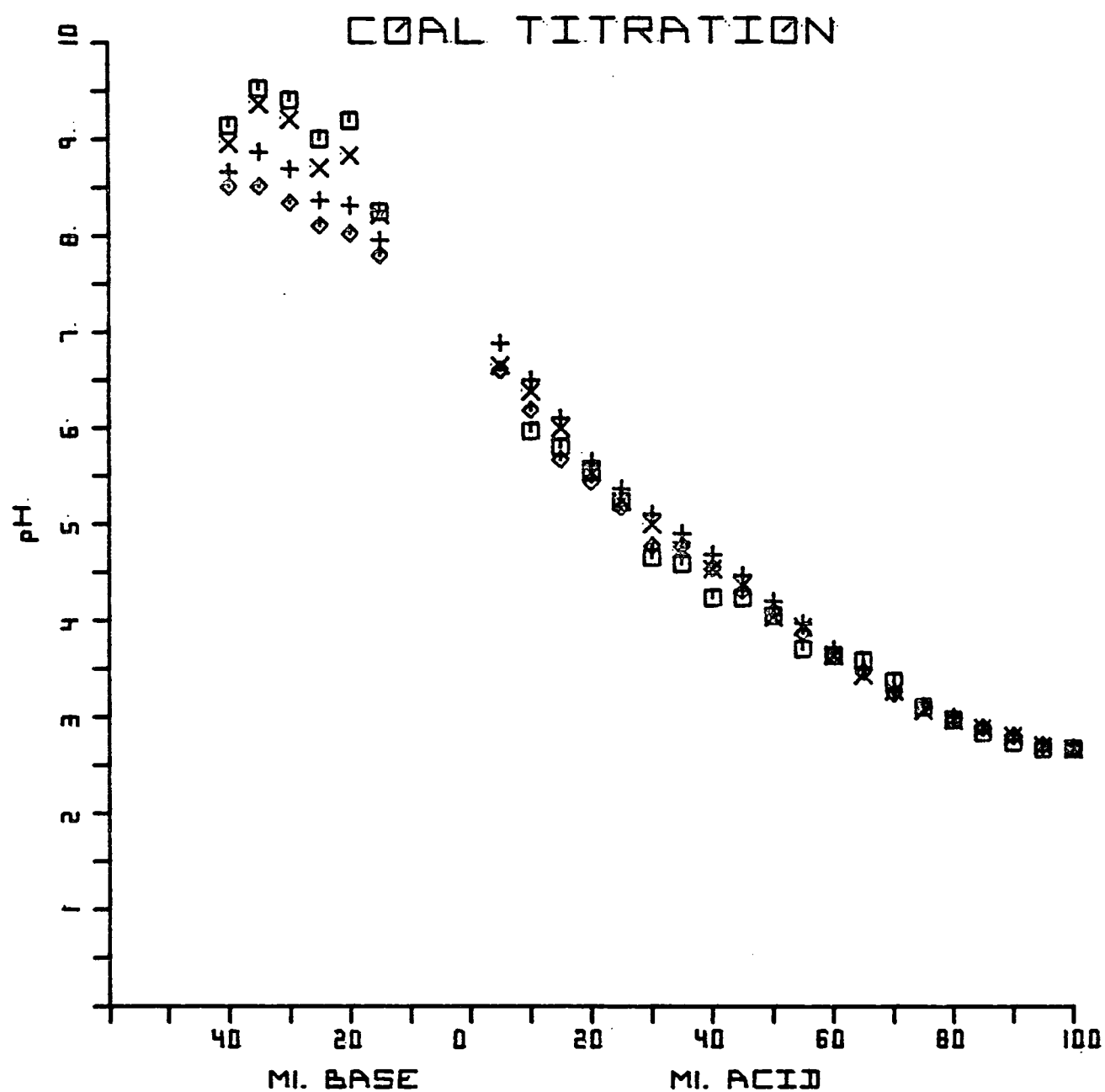
# COAL TITRATION



MI. BASE                    MI. ACID

FIGURE V-C-1:          WESTERN COAL NO. 1
                       SAMPLE SIZE = 2.00 g.
                       HCl  = 0.0106 N
                       NaOH = 0.0096 N

                       ▣ = 0.50  – 1.00  mm PARTICLE SIZE
                       ✕ = 0.25  – 0.50  mm PARTICLE SIZE
                       + = 0.125 – 0.25  mm PARTICLE SIZE
                       ◇ = 0.063 – 0.125 mm PARTICLE SIZE

# FILTER RETENTION STUDY
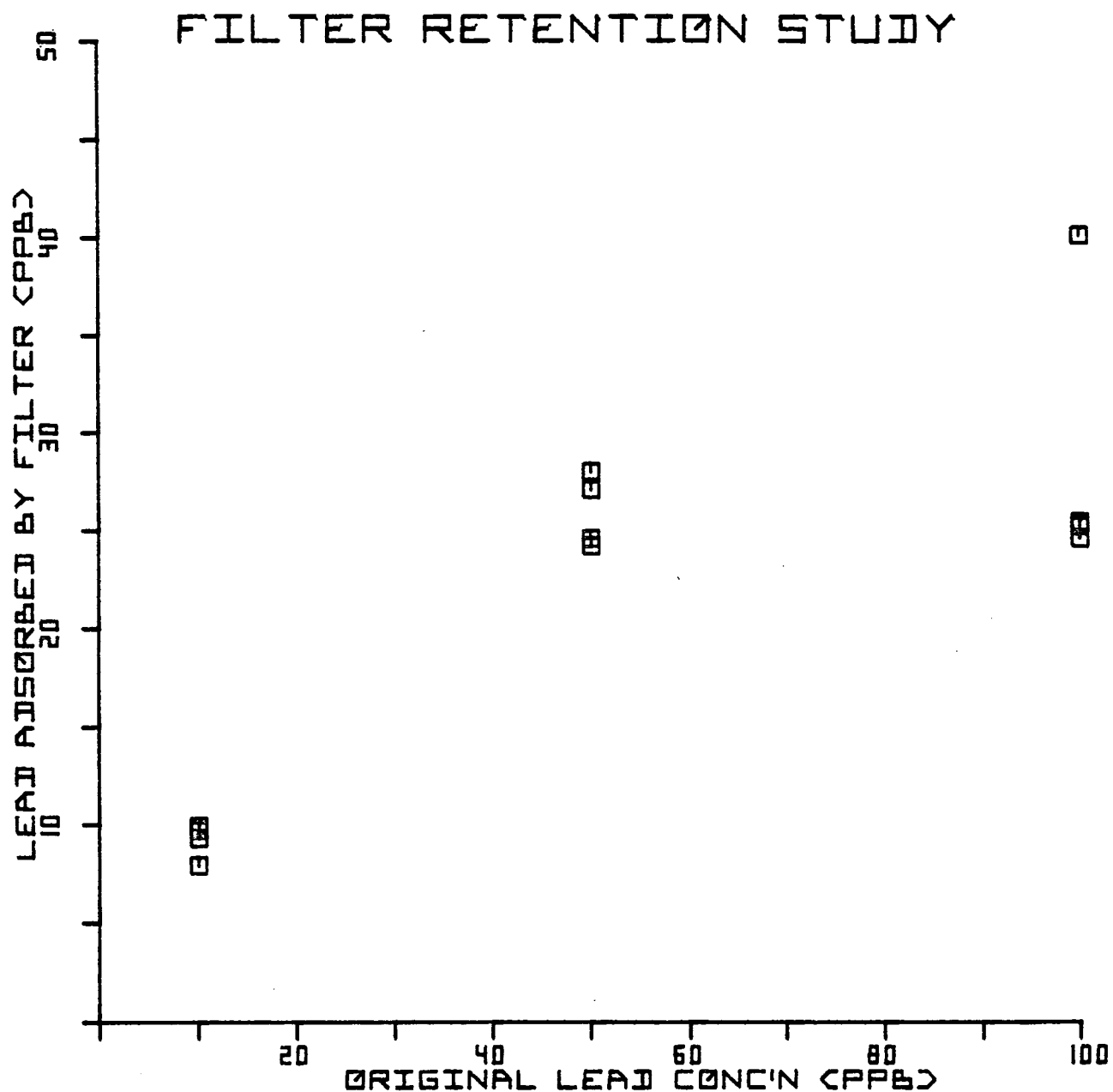


FIGURE V-C-2:  LEAD
  DEIONIZED WATER MEDIUM
  MILLIPORE   0.45   MEMBRANE FILTER
  APROX. 3 MINUTES FILTRATION TIME
  PH RANGE = 5.0-5.5
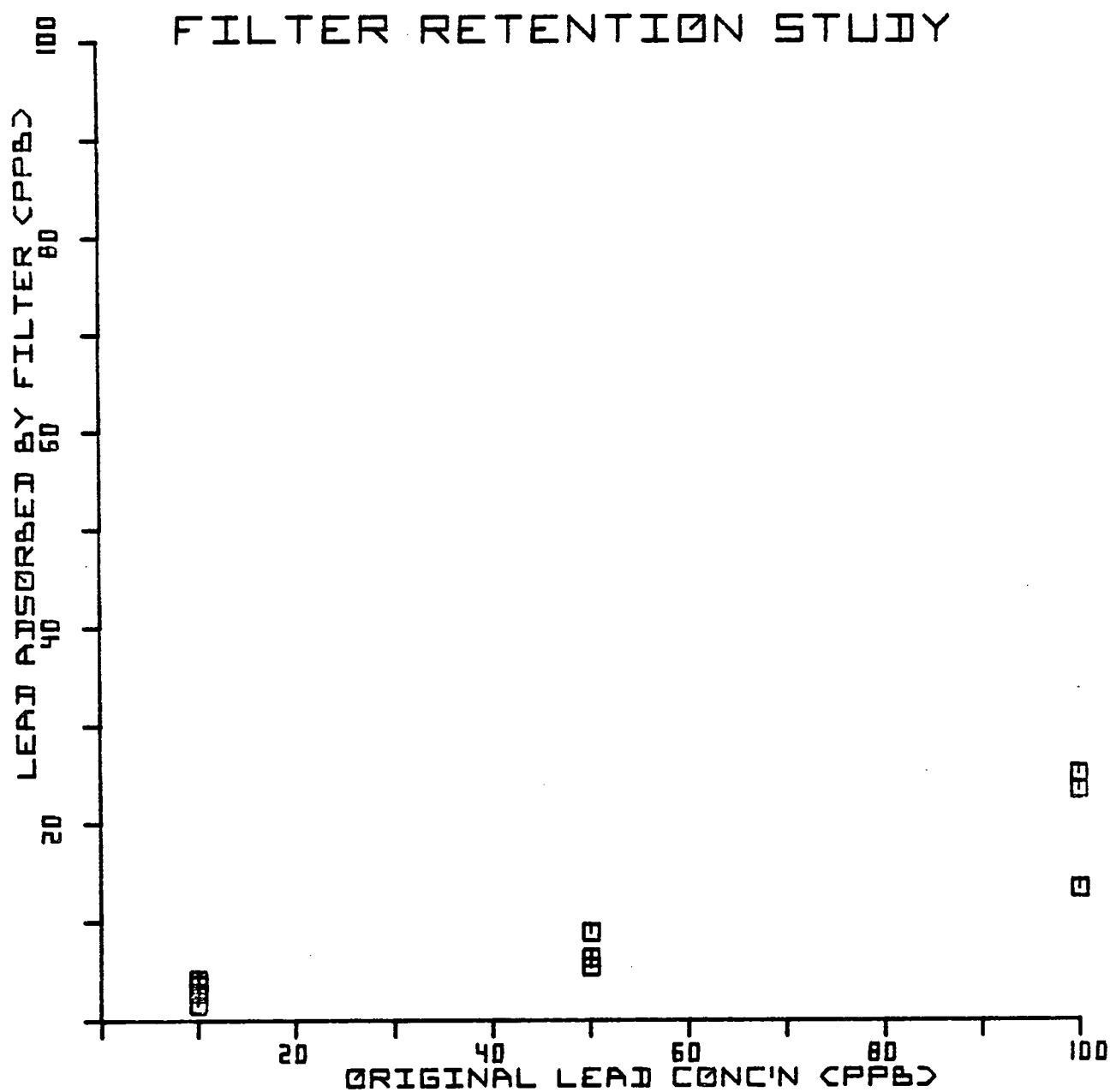
FIGURE V-C-3: LEAD
LAKE WATER MEDIUM
MILLIPORE  0.45   MEMBRANE FILTER
APPROX. 2 MINUTES FILTRATION TIME

# FILTER RETENTION STUDY
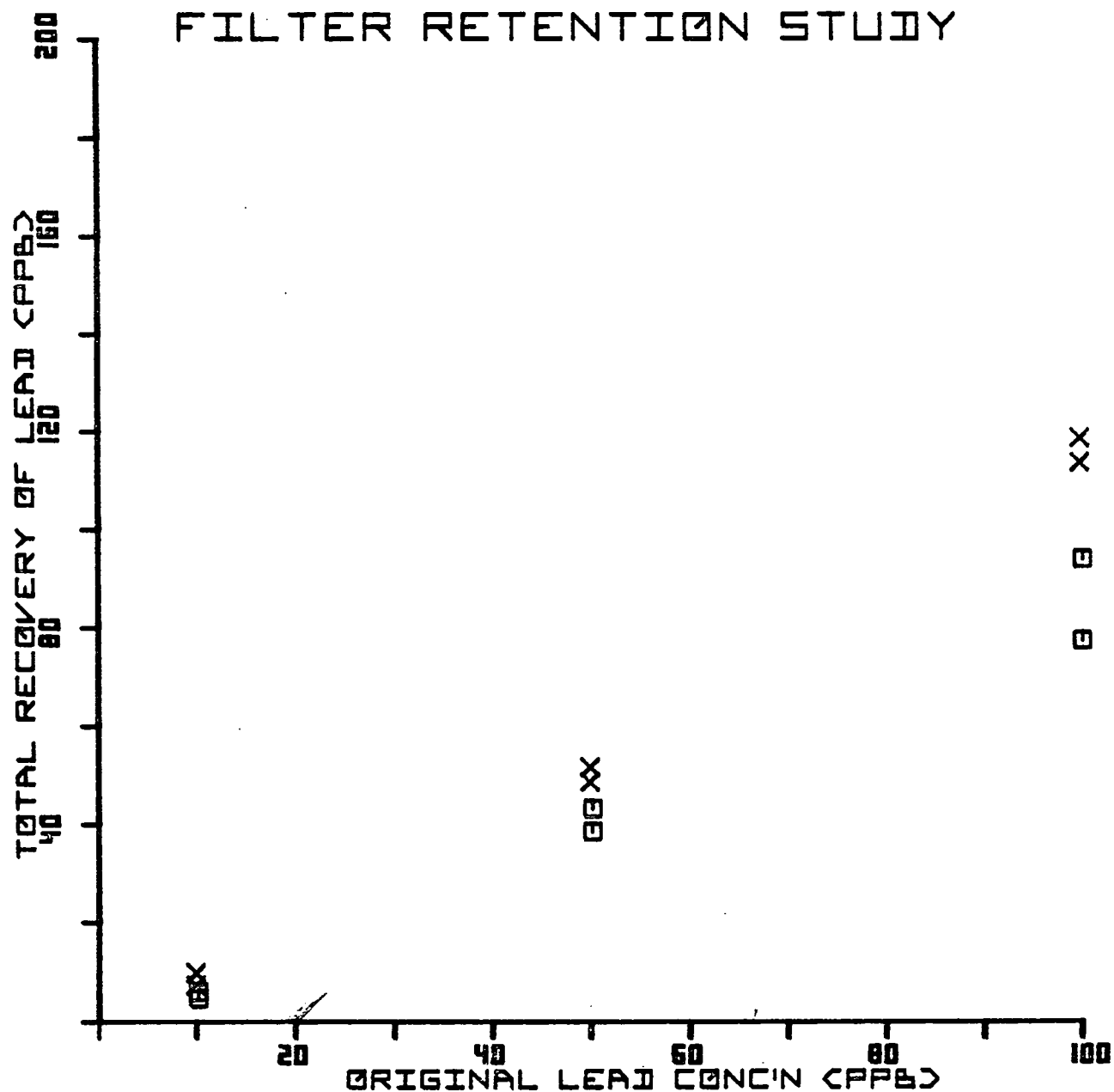


FIGURE V-C-4:  LEAD
DEIONIZED WATER MEDIUM
MILLIPORE ® 0.45 μ MEMBRANE FILTER
APPROX. 3 MINUTE FILTRATION TIME
□ = 0.1 M ALUMINUM ION WASH
X = 0.1 M HYDROCHLORIC ACID WASH

D. MAJOR LEACHING EXPERIMENTS

1. First Factorial Run

a. Experimental--
   The first factorial run consisted of a complete, single factorial experiment on five factors at two levels each. Each portion of the experimental run was sampled at three different times, producing a pure $2^5$ factorial design, overlain with a time parameter to give a pseudo $2^5 \times 3$ factorial design. The time of sampling cannot be taken as a pure factorial level, because samples which are withdrawn during the run cannot be considered truly independent.

   The rationale for the choice of factors and their final experimental levels are described elsewhere in this report (see Section V-A). Factors and their experimental levels as used in this run were as shown in Table V-D-1.

TABLE V-D-1. VARIABLES FOR FACTORIAL RUN

| Factor | | Level 1 | Level 2 |
|---|---|---|---|
| Temperature | (T) | 20°C | 40°C |
| Gas Saturation | (G) | $N_2$ | $O_2$ |
| Rate of Pumping | (R) | 20 ml/min | 80 ml/min |
| Particle Size | (S) | 0.125 to 0.250 mm | 0.500 to 1.00 mm |
| pH | (P) | Unbuffered deionized water whose pH reached 7.3 in the leachate | Sodium acetate-acetic acid buffer whose pH was 4.8 in the leachate |
| Time of Sampling | (H) | 24 hours | 48 hours |

   The factors, when placed in an operational grid, gave 32 separate runs. These runs were set-up four at a time in the leaching system. Since the system consisted of six leaching containers, it was capable of a run of four variables, with two blanks at one servicing of the system. The two blanks were for pure leachate and trace metal-spiked leachate, respectively. It was found that two runs could be accomplished in a one week period, if scheduling of variables was arranged carefully. Thus, a minimum of four weeks was necessary to proceed through the entire set of 32 variables in the factorial run. This, however, gave no opportunity for replication of runs, therefore, certain of the runs were replicated for purposes of analytical control.

   The coal (Western Coal No. 1) was obtained from a coal-car sampling

performed by the Environmental Research Laboratory, Duluth. The sample was visibly wet when obtained.

Sufficient coal for the entire first factorial study was air dried for 24 hours to remove surface moisture. The dried sample was then ground in one pass through a Wiley® Laboratory Mill-Model 4. The exit screen on the Mill's grinding chamber was set to a size of one millimeter. These grindings were then successively mixed by passing them through a stainless steel riffler. The riffler was then used to separate the total sample into 16 representative portions of approximately 10 liters each of ground coal of all grain sizes from one millimeter on down to "fines." These samples were then stored in sealed polyethylene containers. The composite coal samples were sieved as necessary, through specially fabricated stainless steel sieves in order to furnish the appropriate size range of coal granules.

Factorial Levels--
Temperature--The temperatures of 20°C or 40°C were maintained in a 300 liter water bath to $\pm$0.5°C.

Gas Saturation--The leaching system was maintained at two extremum conditions: (a) anoxic, with the circulating leachate being saturated with nitrogen gas, or (b) highly oxygenated, by the use of oxygen to saturate the leachant. The gases were purified, and humidified to minimize evaporation from the system, as described in the section on the structure of the leaching system (Section V-B-6).

Rate of Pumping--A single Masterflex® variable speed pump motor was used to drive a ganged set of six tubing pump heads. One-quarter inch (1/4") flexible silicone tubing (precleaned to remove trace metal impurities) was used in the roller tubing pump heads. Pumping rates of 20 ml/min and 80 ml/min were adopted since they were near the maximum and minimum flow rates of the pump.

Particle Size--The particle size levels were chosen so as to give approximately a 4-to-1 ratio of average particle radius. The Wiley® Laboratory Mill-Model 4, when set according to factory specifications, produced a large fraction in the 0.500 mm to 1.000 mm size range when sorted by the stainless steel sieves, but only minimal amounts of grindings above 1.000 mm size, even with the two millimeter exit screen installed. Thus, the 0.500 to 1.000 mm size was a natural choice for the larger size interval.

Preliminary work on particle size demonstrated that the 0.063 mm to 0.125 mm sized particles did not give good flow rates in leaching experiments. These smaller particles also did not "wet" well when treated with the leachant. The 0.125 mm to 0.500 mm particle sized material, however, gave acceptable flow rates and wetting properties and therefore that size was chosen for the smaller size fraction.

pH--pH was a parameter which had a very large effect on the leaching of metals from coal. Control of acidity levels in the leachant was somewhat difficult to maintain at predetermined settings, due to the fairly high buffer capacity of the western coals.

Early studies, as described elsewhere in this report, showed that one gram of the western coal reacted with about 0.14 millimoles of acetic acid in moving from a pH of 7.3 (unbuffered) to an acetate-acetic acid buffer at a pH of 4.85. High concentrations of the acetate-acetic acid buffer gave matrix problems in the metal ion analyses by atomic absorption spectrophotometry, while low concentrations of buffer in the leachant gave fairly large (and therefore unacceptable) fluctuations in pH over longer periods of time, which made the pH levels in the analyses of variance an unacceptable factor from a statistical standpoint.

A buffer solution which was 0.072 M in acetic acid and 0.028 M in sodium acetate was found to give reasonable pH control on the acidic side. This buffer solution, in contact with western coal stabilized to within 0.1 pH unit after six to twelve hours. This concentration of buffer did not give serious matrix problems during analysis of the metals (see Section V-C-2).

Creation of a buffer of essentially the same capacity on the basic side was not feasible.

Therefore two systems of pH control were adopted for the factorial system:
1. A sodium acetate-acetic acid buffer which stabilized the coal-leachant system at approximately pH 4.7.
2. Unbuffered, deionized water (allowing the coal to serve as its own buffer) which produced an alkaline leachate at a pH of approximately 7.4 in most cases.

The above conditions were within the limits of acceptability of experimental control and for heavy metal analysis.

It should be mentioned that the two systems are not equivalent in ionic strength and are probably not equivalent in absolute buffer capacity. Due to the inherent difficulties in the coal-leachant system, it was felt that pH control was the factor of paramount importance and that the above limits were the best compromise.

Time of Sampling--Preliminary investigations and earlier work demonstrated that there were considerable fluctuations of metal concentrations in the leachate during the very early portions of a run, but that the system stabilized somewhat in the vicinity of 6 hours of running time. Therefore 6, 24 and 48 hours were selected as the three points which would establish any true time trends in metal concentrations in the leachate. These three times established the three levels for the factorial analysis of variance.

b. Results--
Analysis was started on 13 metals for this run, and was completed for the fall factorial set of 96 samples on 5 of these (As, Ba, Cr, Cu and Mn). The remaining 8 metals showed values near or below detection limits in the early analysis. It was therefore decided to analyze these metals (Cd, Co, Pb, Mo, Ni, Se, V and Zn) on a reduced factorial basis. That is, holding gas constant as $N_2$, particle size constant at the 0.125 mm screen fraction

and using only the 24 hour sample. This gave a 2 x 2 x 2 factorial on temperature, rate of pumping and pH.

The results of the reduced factorial are given in Table V-D-7. It can be seen that the values for these metals over these conditions are near or below detection limits. The only obvious trends are (a) Selenium seems to extract better at high pH and (b) Molybdenum seems to extract better at low pH.

Total release data for the complete factorial analyses for (As, Ba, Cr, Cu and Mn) are given in Tables V-D-8 through V-D-12. The $W_{31}$ runs (the 1st half of the third week) showed totally wild results. These runs were repeated and the data for the repeat runs are shown in the table.

In addition some of the copper values for the $W_{11}$ runs were obviously out of line. The $W_{11}$ runs were repeated for the copper and the values shown in Table V-D-11 are the repeat values.

The original statistical analysis of these data were done using a $2^6$ factorial method developed by Yates.[7] The data were later refined using the ANOVAR program from the "Dartmouth Statistical Package." The ANOVAR program allowed a $2^5.3^1$ analysis (time at 3 levels). The ANOVAR results are discussed below:

Arsenic - Using 3rd, 4th and 5th order interactions as a pooled error estimate gives the following variables and interactions as significant:

| | | |
|---|---|---|
| Extremely Significant: | $\propto \ll 0.001$ | T, P, HP |
| Highly Significant: | $\propto < 0.001$ | GRP, H |
| Very Significant: | $\propto < 0.01$ | TG, SH, SHP |
| Significant: | $\propto < 0.025$ | RP, GRS |

These results imply a fairly complex mechanism for leaching. The significant primary variables T, P and H and the first order interaction, HP are clearly shown in Figure V-D-1. The combined effects T, P, H and HP account for 76.7% of the total sum of squares in the analysis.

Barium - It is immediately obvious from Table V-D-9 that pH has a very large effect on barium leaching. The grand mean of the high pH runs is 26.4 ppb of Ba while the grand mean at low pH is 1,580 ppb. That is, an increase of approximately 60 fold is observed in Ba leaching when the system is buffered to high $H^+$ concentrations.

From a statistical viewpoint, these data must be treated as two separate experiments. Otherwise, the lack of a homogeniety of variance would vitiate any analysis of variance treatment. Therefore, the high and low pH runs were split and run on the ANOVAR program as two separate $2^4 \times 3^1$ designs.

The high pH (low $H^+$) runs: Using 3rd and 4th order interactions as a pooled error estimate gives the following variances and interactions as significant:

59

Highly Significant:          $\alpha < 0.001$     R, S
Very Significant:          $\alpha < 0.01$      TGR, H, TG
Significant:              $\alpha < 0.025$     RS, GRS

The main effects R, S and H are outlined in Table V-D-2.

TABLE V-D-2.  MAIN EFFECTS:  BARIUM AT HIGH pH

| Effect | Value | % of Mean |
|---|---|---|
| $\bar{R}_2 - \bar{R}_1$ | -17.79 ppb | -67.51 |
| $\bar{S}_2 - \bar{S}_1$ | -15.29 ppb | -58.03 |
| $\bar{H}_3 - \bar{H}_1$ | -13.75 ppb | -52.18 |

Thus it is seen that leaching is enhanced by slower flow rates, smaller particle size and shorter residence times. The apparently inverse effect of time is probably due to some sort of readsorption process; either on the system walls or on the coal.

The R, S and H effects account for 44.2% of the total sum of squares.

The low pH (high $H^+$) runs: Using 3rd and 4th order interactions as a pooled error estimate gives the following variables and interactions as significant:

Extremely Significant:    $\alpha << 0.001$    T, S
Highly Significant:         $\alpha < 0.001$    R, TG, TGS
Very Significant:          $\alpha < 0.01$     H
Significant:              $\alpha < 0.025$    SH

The main effects T, S, R and H are outlined in Table V-D-3.

TABLE V-D-3.  MAIN EFFECTS:  BARIUM AT LOW pH

| Effect | Value | % of Mean |
|---|---|---|
| $\bar{T}_2 - \bar{T}_1$ | +427.4 ppb | +27.0 |
| $\bar{S}_2 - \bar{S}_1$ | +336.8 ppb | +21.3 |
| $\bar{R}_2 - \bar{R}_1$ | -252.0 ppb | -15.9 |
| $\bar{H}_3 - \bar{H}_1$ | -182.1 ppb | -11.5 |

The T, S, R and H effects account for 65.6% of the total sum of squares.

As in the high pH runs, slower rate of pumping and shorter residence times give greater leaching. Temperature, which was not a main effect in the high pH runs becomes the major variable at low pH. The strange effect of increased leaching with larger particle size is difficult to explain. Most probably it involves a lack of readsorption on the larger particle sizes.

Chromium - Using 3rd, 4th and 5th order interactions as a pooled error estimate gives the following variables and interactions as significant:

| | | |
|---|---|---|
| Extremely Significant: | $\alpha \ll 0.001$ | T, P |
| Highly Significant: | $\alpha < 0.001$ | S, TG, SP |
| Very Significant: | $\alpha < 0.01$ | T, TGR, TS, RS, GSP, HP, THP |
| Significant | $\alpha < 0.025$ | RSP, GP |

The main effects T, R, S and P are outlined in Table V-D-4.

TABLE V-D-4.  MAIN EFFECTS:  CHROMIUM

| Effect | Value | % of Mean |
|---|---|---|
| $\bar{T}_2 - \bar{T}_1$ | +0.1304 ppb | +72.2 |
| $\bar{R}_2 - \bar{R}_1$ | -0.0517 ppb | -28.6 |
| $\bar{S}_2 - \bar{S}_1$ | -0.0983 ppb | -54.4 |
| $\bar{P}_2 - \bar{P}_1$ | -0.1688 ppb | -93.4 |

The leaching of chromium seems to be enhanced at higher temperatures, slower pumping rate, smaller particle size and lower hydrogen ion concentration (higher pH).

Even with the large number of significant interactions, the four main effects account for 36.6% of the total sum of squares.

The grand mean for total release chromium in this experiment was 0.181 ppb. The detection limit for chromium (for unpyrolized tubes) is 0.52. This comparison obviously casts some doubt on the above results. Even so, the main effects are probably real and the large number of significant interactions probably indicates a fairly complex leaching mechanism.

Copper - The results for copper seem to vary on a random basis. The grand mean for the data is 2.41 ppb with an overall standard deviation of 1.75. This yields a Cu value of 95% confidence limits of 2.41 ± 0.36

ppb.

The ANOVAR analysis showed a very confused picture. Using 3rd, 4th and 5th order interactions for an error estimate gives an $s_{error}$ = 1.42 (almost as large as the overall s value). Two interactions: PG and GHP were the most significant at $\alpha<0.025$. With 63 variables and interactions in the design, one would expect about 1.6 effects to show an $\alpha$ this small on a random basis. Therefore, the statistical analysis of the Cu data was terminated at this point.

Manganese - As in the barium results, manganese leaching is very strongly affected by changes in pH. The grand mean for the high pH runs is 0.748 ppb while the grand mean for the low pH runs is 127 ppb. Therefore, the manganese results were split into two $2^4 \times 3^1$ factorial designs for analysis.

The high pH (low $H^+$) runs: Using 3rd and 4th order interactions as a pooled error estimate gives the following varibles and interactions as significant:

Highly Significant:      $\alpha<0.001$     T, S
Very Significant:       $\alpha<0.01$      R, TS

The main effects T, S and R are outlined in Table V-D-5.

TABLE V-D-5.   MAIN EFFECTS:   MANGANESE AT HIGH pH

| Effect | Value | % of Mean |
|---|---|---|
| $\bar{T}_2 - \bar{T}_1$ | +0.438 ppb | +48.6 |
| $\bar{S}_2 - \bar{S}_1$ | -0.513 ppb | -68.6 |
| $\bar{R}_2 - \bar{R}_1$ | -0.254 ppb | -34.0 |

T, S and R account for 68.3% of the total sum of squares.

At high pH, manganese leaching is enhanced by high temperatures, small particle size and slow pumping rate.

The low pH (high $H^+$) runs: Using 3rd and 4th order interactions as a pooled error estimate gives the following variables and interactions as significant:

Extremely Significant:    $\alpha<<0.001$    H
Highly Significant:       $\alpha<0.001$     S
Very Significant:        $\alpha<0.01$     GR, TR

The main effects H and S are given in Table V-D-6.

TABLE V-D-6.  MAIN EFFECTS:  MANGANESE AT LOW pH

| Effect | Value | % of Mean |
|--------|-------|-----------|
| $\overline{H}_3 - \overline{H}_1$ | +38.5 ppb | +30.4 |
| $\overline{S}_2 - \overline{S}_1$ | -12.5 ppb | -9.87 |

The main effects H and S account for 75.5% of the total sum of squares.

At low pH, manganese leaching is enhanced by long leaching times and small particle size.

c.  Overall Results--
    The general picture which emerges here is:
    (1) Most of the variables seem to be significant to some extent.
    (2) pH has a striking effect on barium and manganese.
    (3) The overall mechanism seems to be very complex with considerable variation from metal to metal.

This experiment was probably too complex to design to give much definite information.  It did, however, serve as an excellent springboard to the later experiments in this study.

TABLE V-D-7

RESULTS OF REDUCED FACTORIAL

Raw Data at 24 hr. Sample Time Metal Concentrations in ppb

|  | Cd | Co | Pb | Mo | Ni | Se | V | Zn |
|---|---|---|---|---|---|---|---|---|
| $T_1 R_1 P_1$ | 0.00 | 0.7 | 0.9 | 0.3 | 5.0 | 3.5 | 0.0 | 1.9 |
| $T_2 R_1 P_1$ | 0.01 | 1.4 | 1.9 | 3.2 | 7.9 | 2.4 | 2.5 | 4.2 |
| $T_1 R_2 P_1$ | 0.18 | 0.5 | 1.2 | 0.6 | 1.6 | 2.7 | 0.0 | 0.7 |
| $T_2 R_2 P_1$ | 0.12 | 0.6 | 0.4 | 2.6 | 7.9 | 3.1 | 0.0 | 1.9 |
| $T_1 R_1 P_2$ | 0.02 | 1.0 | 0.1 | 10.0 | 5.5 | 1.2 | 2.5 | 5.0 |
| $T_2 R_1 P_2$ | 0.07 | 0.7 | 0.5 | 11.3 | 3.4 | 1.2 | 0.0 | 2.6 |
| $T_1 R_2 P_2$ | 0.16 | 0.3 | 0.0 | 10.7 | 21.1 | 1.2 | 0.0 | 0.0 |
| $T_2 R_2 P_2$ | 0.57 | 5.4 | 0.2 | 10.0 | 2.9 | 1.0 | 0.0 | 0.2 |
| Detection Limit | 0.08 | 1.0 | 0.47 | 6.6 | 4.1 | --- | 2.4 | 0.18 |

TABLE V-D-8

FIRST FACTORIAL ANALYSIS

TOTAL RELEASE ARSENIC

| Week & Bottle | Factor Code | 6 Hr | 24 Hr | 48 Hr |
|---|---|---|---|---|
| $W_{41}\text{-}B_4$ | $T_1G_1R_1S_1P_1$ | 1.20 | 0.56 | 0.88 |
| $W_{11}\text{-}B_1$ | $T_2G_1R_1S_1P_1$ | 2.80 | 2.44 | 2.35 |
| $W_{21}\text{-}B_4$ | $T_1G_2R_1S_1P_1$ | 1.50 | 0.87 | 1.11 |
| $W_{31}\text{-}B_1R*$ | $T_2G_2R_1S_1P_1$ | 2.30 | 0.91 | 1.45 |
| $W_{22}\text{-}B_1$ | $T_1G_1R_2S_1P_1$ | 1.00 | 0.55 | 0.57 |
| $W_{32}\text{-}B_4$ | $T_2G_1R_2S_1P_1$ | 2.00 | 1.10 | 1.15 |
| $W_{42}\text{-}B_1$ | $T_1G_2R_2S_1P_1$ | 0.80 | 0.74 | 0.37 |
| $W_{12}\text{-}B_4$ | $T_2G_2R_2S_1P_1$ | 1.30 | 1.06 | 1.31 |
| $W_{41}\text{-}B_1$ | $T_1G_1R_1S_2P_1$ | 1.10 | 1.85 | 0.64 |
| $W_{11}\text{-}B_4$ | $T_2G_1R_1S_2P_1$ | 1.50 | 2.17 | 1.38 |
| $W_{21}\text{-}B_1$ | $T_1G_2R_1S_2P_1$ | 1.00 | 1.05 | 0.50 |
| $W_{31}\text{-}B_4R*$ | $T_2G_2R_1S_2P_1$ | 1.50 | 1.37 | 1.24 |
| $W_{22}\text{-}B_4$ | $T_1G_1R_2S_2P_1$ | 0.80 | 0.64 | 0.67 |
| $W_{32}\text{-}B_1$ | $T_2G_1R_2S_2P_1$ | 1.10 | 0.75 | 0.69 |
| $W_{42}\text{-}B_4$ | $T_1G_2R_2S_2P_1$ | 0.40 | 1.02 | 0.67 |
| $W_{12}\text{-}B_1$ | $T_2G_2R_2S_2P_1$ | 2.00 | 2.50 | 1.02 |
| $W_{41}\text{-}B_2$ | $T_1G_1R_1S_1P_2$ | 1.50 | 1.87 | 1.76 |
| $W_{11}\text{-}B_3$ | $T_2G_1R_1S_1P_2$ | 2.30 | 2.51 | 4.13 |
| $W_{21}\text{-}B_2$ | $T_1G_2R_1S_1P_2$ | 2.60 | 2.13 | 3.33 |
| $W_{31}\text{-}B_3R*$ | $T_2G_2R_1S_1P_2$ | 2.90 | 3.04 | 4.49 |
| $W_{22}\text{-}B_3$ | $T_1G_1R_2S_1P_2$ | 2.20 | 3.11 | 2.26 |
| $W_{32}\text{-}B_2$ | $T_2G_1R_2S_1P_2$ | 3.60 | 3.38 | 4.04 |
| $W_{42}\text{-}B_3$ | $T_1G_2R_2S_1P_2$ | 2.00 | 2.20 | 3.20 |
| $W_{12}\text{-}B_2$ | $T_2G_2R_2S_1P_2$ | 2.00 | 2.80 | 2.33 |
| $W_{41}\text{-}B_3$ | $T_1G_1R_1S_2P_2$ | 1.10 | 1.55 | 2.53 |
| $W_{11}\text{-}B_2$ | $T_2G_1R_1S_2P_2$ | 2.10 | 3.60 | 6.08 |
| $W_{21}\text{-}B_3$ | $T_1G_2R_1S_2P_2$ | 1.80 | 2.19 | 2.89 |
| $W_{31}\text{-}B_2R*$ | $T_2G_2R_1S_2P_2$ | 2.30 | 3.01 | 4.06 |
| $W_{22}\text{-}B_2$ | $T_1G_1R_2S_2P_2$ | 1.70 | 2.38 | 3.40 |
| $W_{32}\text{-}B_3$ | $T_2G_1R_2S_2P_2$ | 2.90 | 3.34 | 4.10 |
| $W_{42}\text{-}B_2$ | $T_1G_2R_2S_2P_2$ | 1.80 | 1.89 | 2.88 |
| $W_{12}\text{-}B_3$ | $T_2G_2R_2S_2P_2$ | 2.00 | 2.50 | 4.52 |

*Values from replicate run were used.

TABLE V-D-9

FIRST FACTORIAL ANALYSIS

TOTAL RELEASE BARIUM

| Week & Bottle | Factor Code | | 6 Hr | 24 Hr | 48 Hr |
|---|---|---|---|---|---|
| $W_{41}$-$B_4$ | $T_1G_1R_1S_1P_1$ | | 45 | 27 | 29 |
| $W_{11}$-$B_1$ | $T_2G_1R_1S_1P_1$ | | 90 | 60 | 67 |
| $W_{21}$-$B_4$ | $T_1G_2R_1S_1P_1$ | | 65 | 48 | 36 |
| $W_{31}$-$B_1$R* | $T_2G_2R_1S_1P_1$ | | 30 | 32 | 33 |
| $W_{22}$-$B_1$ | $T_1G_1R_2S_1P_1$ | | 15 | 16 | 17 |
| $W_{32}$-$B_4$ | $T_2G_1R_2S_1P_1$ | | 25 | 26 | 28 |
| $W_{42}$-$B_1$ | $T_1G_2R_2S_1P_1$ | | 15 | 6 | 11 |
| $W_{12}$-$B_4$ | $T_2G_2R_2S_1P_1$ | High pH | 40 | 27 | 28 |
| $W_{41}$-$B_1$ | $T_1G_1R_1S_2P_1$ | | 25 | 11 | 12 |
| $W_{11}$-$B_4$ | $T_2G_1R_1S_2P_1$ | | 45 | 17 | 8 |
| $W_{21}$-$B_1$ | $T_1G_2R_1S_2P_1$ | | 70 | 24 | 25 |
| $W_{31}$-$B_4$R* | $T_2G_2R_1S_2P_1$ | | 26 | 10 | 11 |
| $W_{22}$-$B_4$ | $T_1G_1R_2S_2P_1$ | | 30 | 17 | 7 |
| $W_{32}$-$B_1$ | $T_2G_1R_2S_2P_1$ | | 25 | 21 | 12 |
| $W_{42}$-$B_4$ | $T_1G_2R_2S_2P_1$ | | 5 | 10 | 6 |
| $W_{12}$-$B_1$ | $T_2G_2R_2S_2P_1$ | | 10 | 11 | 11 |
| $W_{41}$-$B_2$ | $T_1G_1R_1S_1P_2$ | | 1470 | 1125 | 1035 |
| $W_{11}$-$B_3$ | $T_2G_1R_1S_1P_2$ | | 2150 | 1810 | 1660 |
| $W_{21}$-$B_2$ | $T_1G_2R_1S_1P_2$ | | 1570 | 1290 | 1100 |
| $W_{31}$-$B_3$R* | $T_2G_2R_1S_1P_2$ | | 1650 | 1560 | 1675 |
| $W_{22}$-$B_3$ | $T_1G_1R_2S_1P_2$ | | 1170 | 1150 | 895 |
| $W_{32}$-$B_2$ | $T_2G_1R_2S_1P_2$ | | 1710 | 1325 | 1440 |
| $W_{42}$-$B_3$ | $T_1G_2R_2S_1P_2$ | | 1300 | 1155 | 860 |
| $W_{12}$-$B_2$ | $T_2G_2R_2S_1P_2$ | Low pH | 1770 | 1660 | 1350 |
| $W_{41}$-$B_3$ | $T_1G_1R_1S_2P_2$ | | 1520 | 1365 | 1520 |
| $W_{11}$-$B_2$ | $T_2G_1R_1S_2P_2$ | | 2260 | 2495 | 2490 |
| $W_{21}$-$B_3$ | $T_1G_2R_1S_2P_2$ | | 2070 | 2145 | 1815 |
| $W_{31}$-$B_2$R* | $T_2G_2R_1S_2P_2$ | | 1700 | 1695 | 1775 |
| $W_{22}$-$B_2$ | $T_1G_1R_2S_2P_2$ | | 1390 | 1290 | 1350 |
| $W_{32}$-$B_3$ | $T_2G_1R_2S_2P_2$ | | 2240 | 2060 | 1970 |
| $W_{42}$-$B_2$ | $T_1G_2R_2S_2P_2$ | | 1350 | 1420 | 1435 |
| $W_{12}$-$B_3$ | $T_2G_2R_2S_2P_2$ | | 1570 | 1430 | 1605 |

*Values from replicate run were used.

TABLE V-D-10

FIRST FACTORIAL ANALYSIS

TOTAL RELEASE CHROMIUM

| Week & Bottle | Factor Code | 6 Hr | 24 Hr | 48 Hr |
|---|---|---|---|---|
| $W_{41}-B_4$ | $T_1G_1R_1S_1P_1$ | 0.40 | 0.42 | 0.54 |
| $W_{11}-B_1$ | $T_2G_1R_1S_1P_1$ | 0.50 | 0.32 | 0.84 |
| $W_{21}-B_4$ | $T_1G_2R_1S_1P_1$ | 0.20 | 0.21 | 0.22 |
| $W_{31}-B_1R*$ | $T_2G_2R_1S_1P_1$ | 0.50 | 0.52 | 0.95 |
| $W_{22}-B_1$ | $T_1G_1R_2S_1P_1$ | 0.20 | 0.21 | 0.21 |
| $W_{32}-B_4$ | $T_2G_1R_2S_1P_1$ | 0.40 | 0.22 | 0.83 |
| $W_{42}-B_1$ | $T_1G_2R_2S_1P_1$ | 0.00 | 0.20 | 0.01 |
| $W_{12}-B_4$ | $T_2G_2R_2S_1P_1$ | 0.30 | 0.31 | 0.33 |
| $W_{41}-B_1$ | $T_1G_1R_1S_2P_1$ | 0.20 | 0.21 | 0.22 |
| $W_{11}-B_4$ | $T_2G_1R_1S_2P_1$ | 0.00 | 0.00 | 0.00 |
| $W_{21}-B_1$ | $T_1G_2R_1S_2P_1$ | 0.20 | 0.01 | 0.01 |
| $W_{31}-B_4R*$ | $T_2G_2R_1S_2P_1$ | 0.20 | 0.21 | 0.22 |
| $W_{22}-B_4$ | $T_1G_1R_2S_2P_1$ | 0.20 | 0.21 | 0.22 |
| $W_{32}-B_1$ | $T_2G_1R_2S_2P_1$ | 0.20 | 0.21 | 0.22 |
| $W_{42}-B_4$ | $T_1G_2R_2S_2P_1$ | 0.00 | 0.20 | 0.01 |
| $W_{12}-B_1$ | $T_2G_2R_2S_2P_1$ | 0.20 | 0.21 | 0.52 |
| $W_{41}-B_2$ | $T_1G_1R_1S_1P_2$ | 0.00 | 0.20 | 0.01 |
| $W_{11}-B_3$ | $T_2G_1R_1S_1P_2$ | 0.00 | 0.00 | 0.00 |
| $W_{21}-B_2$ | $T_1G_2R_1S_1P_2$ | 0.00 | 0.00 | 0.20 |
| $W_{31}-B_3R*$ | $T_2G_2R_1S_1P_2$ | 0.00 | 0.70 | 0.23 |
| $W_{22}-B_3$ | $T_1G_1R_2S_1P_2$ | 0.00 | 0.00 | 0.00 |
| $W_{32}-B_2$ | $T_2G_1R_2S_1P_2$ | 0.20 | 0.01 | 0.01 |
| $W_{42}-B_3$ | $T_1G_2R_2S_1P_2$ | 0.00 | 0.00 | 0.00 |
| $W_{12}-B_2$ | $T_2G_2R_2S_1P_2$ | 0.20 | 0.21 | 0.22 |
| $W_{41}-B_3$ | $T_1G_1R_1S_2P_2$ | 0.00 | 0.40 | 0.22 |
| $W_{11}-B_2$ | $T_2G_1R_1S_2P_2$ | 0.20 | 0.01 | 0.01 |
| $W_{21}-B_3$ | $T_1G_2R_1S_2P_2$ | 0.00 | 0.00 | 0.00 |
| $W_{31}-B_2R*$ | $T_2G_2R_1S_2P_2$ | 0.20 | 0.21 | 0.22 |
| $W_{22}-B_2$ | $T_1G_1R_2S_2P_2$ | 0.00 | 0.00 | 0.00 |
| $W_{32}-B_3$ | $T_2G_1R_2S_2P_2$ | 0.20 | 0.21 | 0.02 |
| $W_{42}-B_2$ | $T_1G_2R_2S_2P_2$ | 0.00 | 0.00 | 0.00 |
| $W_{12}-B_3$ | $T_2G_2R_2S_2P_2$ | 0.20 | 0.31 | 0.02 |

*Values from replicate run used.

TABLE V-D-11

FIRST FACTORIAL ANALYSIS

TOTAL RELEASE COPPER

| Week & Bottle | Factor Code | 6 Hr | 24 Hr | 48 Hr |
|---|---|---|---|---|
| $W_{41}$-$B_4$ | $T_1G_1R_1S_1P_1$ | 2.7 | 3.0 | 2.1 |
| $W_{11}$-$B_1$R* | $T_2G_1R_1S_1P_1$ | 1.1 | 3.8 | 2.2 |
| $W_{21}$-$B_4$ | $T_1G_2R_1S_1P_1$ | 1.3 | 1.4 | 0.7 |
| $W_{31}$-$B_1$R* | $T_2G_2R_1S_1P_1$ | 2.8 | 2.1 | 2.4 |
| $W_{22}$-$B_1$ | $T_1G_1R_2S_1P_1$ | 7.7 | 2.7 | 2.3 |
| $W_{32}$-$B_4$ | $T_2G_1R_2S_1P_1$ | 1.9 | 2.5 | 2.1 |
| $W_{42}$-$B_1$ | $T_1G_2R_2S_1P_1$ | 3.2 | 1.7 | 2.1 |
| $W_{12}$-$B_4$ | $T_2G_2R_2S_1P_1$ | 2.2 | 1.4 | 1.2 |
| $W_{41}$-$B_1$ | $T_1G_1R_1S_2P_1$ | 3.2 | 1.3 | 1.7 |
| $W_{11}$-$B_4$R* | $T_2G_1R_1S_2P_1$ | 1.8 | 1.7 | 2.5 |
| $W_{21}$-$B_1$ | $T_1G_2R_1S_2P_1$ | 4.2 | 2.5 | 1.6 |
| $W_{31}$-$B_4$R* | $T_2G_2R_1S_2P_1$ | 1.3 | 1.7 | 1.4 |
| $W_{22}$-$B_4$ | $T_1G_1R_2S_2P_1$ | 1.3 | 1.1 | 1.1 |
| $W_{32}$-$B_1$ | $T_2G_1R_2S_2P_1$ | 3.5 | 3.5 | 1.7 |
| $W_{42}$-$B_4$ | $T_1G_2R_2S_2P_1$ | 1.5 | 1.6 | 1.2 |
| $W_{12}$-$B_1$ | $T_2G_2R_2S_2P_1$ | 1.7 | 1.4 | 4.2 |
| $W_{41}$-$B_2$ | $T_1G_1R_1S_1P_2$ | 2.1 | 2.5 | 3.2 |
| $W_{11}$-$B_3$R* | $T_2G_1R_1S_1P_2$ | 2.0 | 3.2 | 6.7 |
| $W_{21}$-$B_2$ | $T_1G_2R_1S_1P_2$ | 3.5 | 2.8 | 1.4 |
| $W_{31}$-$B_3$R* | $T_2G_2R_1S_1P_2$ | 1.8 | 2.1 | 3.2 |
| $W_{22}$-$B_3$ | $T_1G_1R_2S_1P_2$ | 1.3 | 1.6 | 1.6 |
| $W_{32}$-$B_2$ | $T_2G_1R_2S_1P_2$ | 1.9 | 1.6 | 2.1 |
| $W_{42}$-$B_3$ | $T_1G_2R_2S_1P_2$ | 1.8 | 1.9 | 1.1 |
| $W_{12}$-$B_2$ | $T_2G_2R_2S_1P_2$ | 12.9 | 2.1 | 2.7 |
| $W_{41}$-$B_3$ | $T_1G_1R_1S_2P_2$ | 1.8 | 2.4 | 3.5 |
| $W_{11}$-$B_2$R* | $T_2G_1R_1S_2P_2$ | 1.1 | 2.1 | 0.9 |
| $W_{21}$-$B_3$ | $T_1G_2R_1S_2P_2$ | 2.0 | 1.8 | 2.2 |
| $W_{31}$-$B_2$R* | $T_2G_2R_1S_2P_2$ | 3.2 | 2.2 | 2.8 |
| $W_{22}$-$B_2$ | $T_1G_1R_2S_2P_2$ | 1.6 | 1.2 | 1.9 |
| $W_{32}$-$B_3$ | $T_2G_1R_2S_2P_2$ | 1.3 | 1.8 | 2.5 |
| $W_{42}$-$B_2$ | $T_1G_2R_2S_2P_2$ | 2.5 | 1.4 | 1.4 |
| $W_{12}$-$B_3$ | $T_2G_2R_2S_2P_2$ | 10.8 | 3.0 | 3.5 |

*Values from replicate runs used.

## TABLE V-D-12

### FIRST FACTORIAL ANALYSIS
### TOTAL RELEASE MANGANESE

| Week & Bottle | Factor Code | | 6 Hr | 24 Hr | 48 Hr |
|---|---|---|---|---|---|
| $W_{41}\text{-}B_4$ | $T_1G_1R_1S_1P_1$ | | 0.8 | 0.9 | 1.1 |
| $W_{11}\text{-}B_1$ | $T_2G_1R_1S_1P_1$ | | 1.4 | 1.5 | 2.4 |
| $W_{21}\text{-}B_4$ | $T_1G_2R_1S_1P_1$ | | 0.8 | 0.7 | 0.7 |
| $W_{31}\text{-}B_1R*$ | $T_2G_2R_1S_1P_1$ | | 1.8 | 1.1 | 1.3 |
| $W_{22}\text{-}B_1$ | $T_1G_1R_2S_1P_1$ | | 0.9 | 0.5 | 0.5 |
| $W_{32}\text{-}B_4$ | $T_2G_1R_2S_1P_1$ | | 0.8 | 1.0 | 1.3 |
| $W_{42}\text{-}B_1$ | $T_1G_2R_2S_1P_1$ | High pH | 0.4 | 0.3 | 0.5 |
| $W_{12}\text{-}B_4$ | $T_2G_2R_2S_1P_1$ | | 1.1 | 1.1 | 1.2 |
| $W_{41}\text{-}B_1$ | $T_1G_1R_1S_2P_1$ | | 0.5 | 0.4 | 0.4 |
| $W_{11}\text{-}B_4$ | $T_2G_1R_1S_2P_1$ | | 0.7 | 0.4 | 0.6 |
| $W_{21}\text{-}B_1$ | $T_1G_2R_1S_2P_1$ | | 0.7 | 0.3 | 0.5 |
| $W_{31}\text{-}B_4R*$ | $T_2G_2R_1S_2P_1$ | | 0.5 | 0.8 | 0.7 |
| $W_{22}\text{-}B_4$ | $T_1G_1R_2S_2P_1$ | | 0.5 | 0.3 | 0.4 |
| $W_{32}\text{-}B_1$ | $T_2G_1R_2S_2P_1$ | | 0.5 | 0.5 | 0.6 |
| $W_{42}\text{-}B_4$ | $T_1G_2R_2S_2P_1$ | | 0.2 | 0.2 | 0.2 |
| $W_{12}\text{-}B_1$ | $T_2G_2R_2S_2P_1$ | | 0.5 | 0.5 | 0.9 |
| $W_{41}\text{-}B_2$ | $T_1G_1R_1S_1P_2$ | | 120 | 144 | 197 |
| $W_{11}\text{-}B_3$ | $T_2G_1R_1S_1P_2$ | | 113 | 131 | 147 |
| $W_{21}\text{-}B_2$ | $T_1G_2R_1S_1P_2$ | | 114 | 134 | 142 |
| $W_{31}\text{-}B_3R*$ | $T_2G_2R_1S_1P_2$ | | 105 | 129 | 140 |
| $W_{22}\text{-}B_3$ | $T_1G_1R_2S_1P_2$ | | 111 | 124 | 135 |
| $W_{32}\text{-}B_2$ | $T_2G_1R_2S_1P_2$ | | 117 | 127 | 158 |
| $W_{42}\text{-}B_3$ | $T_1G_2R_2S_1P_2$ | | 118 | 139 | 146 |
| $W_{12}\text{-}B_2$ | $T_2G_2R_2S_1P_2$ | Low pH | 105 | 139 | 154 |
| $W_{41}\text{-}B_3$ | $T_1G_1R_1S_2P_2$ | | 114 | 126 | 145 |
| $W_{11}\text{-}B_2$ | $T_2G_1R_1S_2P_2$ | | 91 | 116 | 138 |
| $W_{21}\text{-}B_3$ | $T_1G_2R_1S_2P_2$ | | 96 | 121 | 133 |
| $W_{31}\text{-}B_2R*$ | $T_2G_2R_1S_2P_2$ | | 93 | 124 | 134 |
| $W_{22}\text{-}B_2$ | $T_1G_1R_2S_2P_2$ | | 99 | 112 | 128 |
| $W_{32}\text{-}B_3$ | $T_2G_1R_2S_2P_2$ | | 102 | 122 | 133 |
| $W_{42}\text{-}B_2$ | $T_1G_2R_2S_2P_2$ | | 96 | 135 | 142 |
| $W_{12}\text{-}B_3$ | $T_2G_2R_2S_2P_2$ | | 106 | 138 | 144 |

*Values from replicate run used.

# pH AND TIME INTERACTION
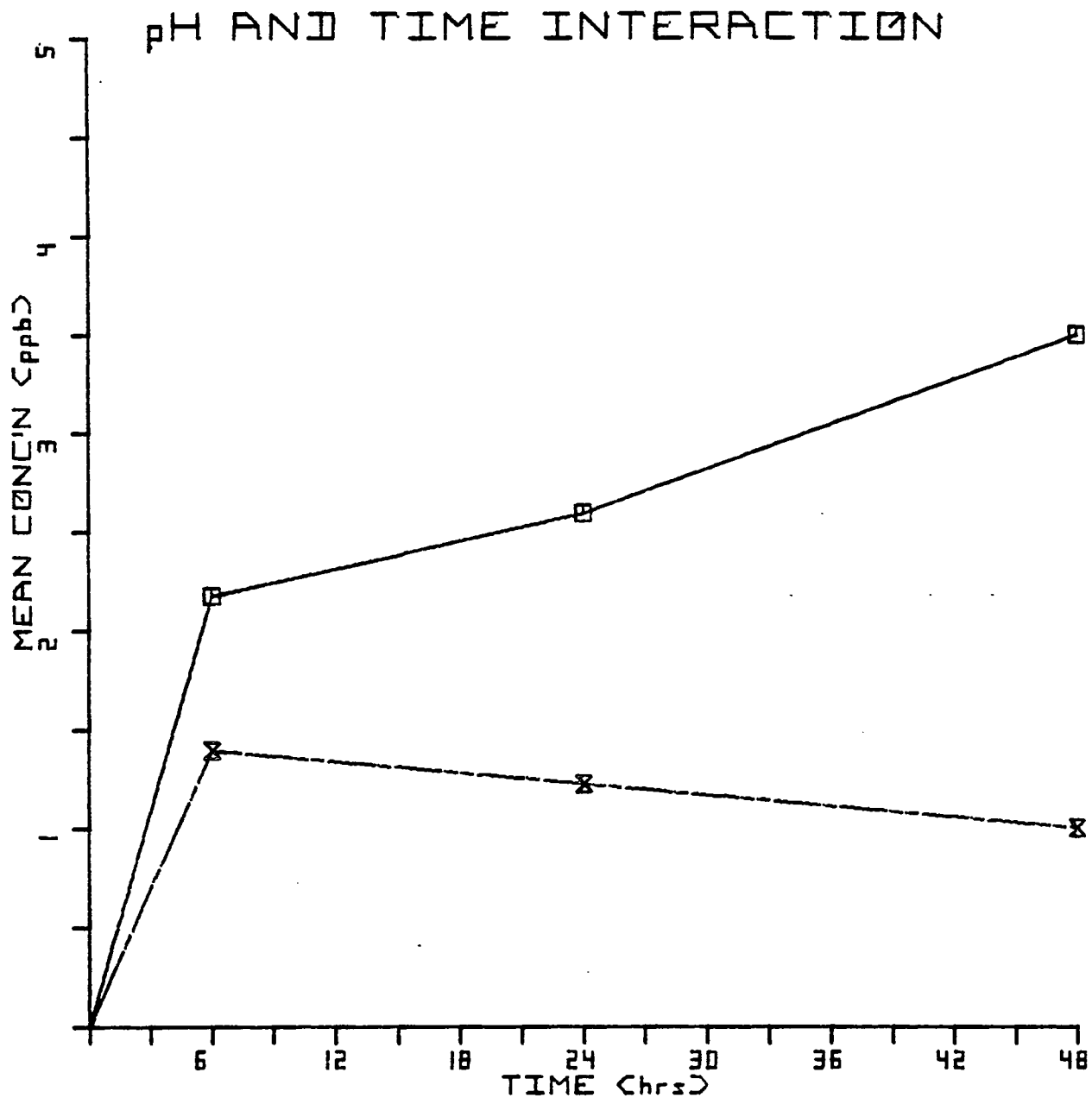
FIGURE V-D-1:    ARSENIC-FIRST FACTORIAL RUN
WESTERN COAL NO.1 <0.25-0.50 mm>
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO = 0.2 g./1.0 g.
OXYGEN AND NITROGEN ATMOSPHERES
TOTAL RELEASE
___□___LOW pH  CONDITIONS
___☒___HIGH pH CONDITIONS

## 2. Continuous Flow Releaching Runs

a. Experimental--

The purpose of this study was to determine the quantity of metal ion which would be mobilized by sequential changes in fresh leachant.

The continuous flow releaching experiments were done in the set-up which was employed in the first factorial experiment and the releaching factorial experiment (see appropriate sections of this report).

Experimental conditions were held as listed in Table V-D-13.

TABLE V-D-13. EXPERIMENTAL CONDITIONS FOR CONTINUOUS FLOW RELEACHING

| Variable | Set 1 | Set 2 |
|---|---|---|
| Coal | Western Coal No. 1 | Same |
| Particle Size | 0.250 - 0.500 mm | Same |
| Leachant | Deionized Water | Acetate Buffer |
| Flow Rate | 20 ml/min | Same |
| Temperature | 40°C | Same |
| Sampling Times | 48, 96, 144, 192 hrs. | Same |
| Leachant Replacement | 48, 96, 144 hrs. | Same |

Coal -  Western Coal No. 1 was dried, ground and sieved as previously described. See Section V-b.

Leachant -  Two different ypes of leachant were used in this experiment:
1. Deionized Water:  See Section V-B-5.
2. Acetate Buffer:  See Section V-C-2

The different leachants were used to determine the difference in behavior of the coal at two levels of pH.

Procedure -  Duplicate samples were prepared, containing 200 grams of Western Coal No. 1 (0.250 - 0.500 mm size) and 1000 ml of the two types of leachant. This allowed replicate runs to be performed with each leachant system, thus giving better analytical control for statistical purposes. Samples were withdrawn, leachant replaced and the stabilized leachates were analyzed by flameless atomic absorption spectrophotometry.[1, 2, 10, 11, 15, 16]

71

Samples were taken at 48, 96, 144 and 192 hrs (termination of the experiment).  At each sampling, 800 ml of leachate was removed and replaced with an equivalent volume of fresh leachant of the appropriate type.

A portion of the fresh leachate was used for pH determination.  Other portions of the leachate were filtered, with suction, through a 0.45 micron membrane filter and acidified with ultra-pure nitric acid to stabilize them for storage and analysis.

b.  Results and Discussion--
Total release values versus time are plotted in Figs. V-D-2 through V-D-21.  For each metal, the deionized water leaching graph is followed by the graph for the acetate buffer leaching.

The nickel samples were lost to analysis because of nickel contamination.  Lead and vanadium values were zero or near zero throughout and not plotted.

The main features of these results are:  (1) metal continues to be removed from the coal with repeated leachings (except perhaps for selenium in the acetate buffer), (2) greater amounts of metal are leached by the low pH (acetate buffer) leachant (except for copper, selenium and zinc), (3) excellent agreement between the paired runs is obtained (except for chromium and manganese in deionized water and copper and selenium in the acetate buffer).  Even the worst cases are not too far off considering the inherent errors of this type of system, (4) the results agree with the results obtained in the shaker releaching work (see Table V-D-14).

While the agreement between shaker and continuous flow experiments is by no means exact, the general consistency certainly implies that shaker work would make a fair predictor for continuous flow work.

For further implications of these results, see the discussion section of the shaker releach work.

72

TABLE V-D-14. COMPARISON OF THE SHAKER RELEACHING STUDY WITH THE CONTINUOUS FLOW RELEACHING STUDY 192 HOUR VALUES (TOTAL RELEASE IN ppb).

| Metal | Deionized Water | | Acetate Buffer | |
|-------|--------|---------------------|--------|---------------------|
|       | Shaker | Continuous Flow (Ave.) | Shaker | Continuous Flow (Ave.) |
| As    | 3.5    | 3.0                 | 11.3   | 25.1                |
| Ba    | 124    | 54.4                | 4002   | 5748                |
| Cd    | 1.6    | 1.9                 | 5.2    | 4.3                 |
| Cr    | 2.0    | 0.7                 | 1.1    | 2.5                 |
| Co    | 0.9    | 0.8                 | 4.8    | 4.9                 |
| Cu    | 3.4    | 8.1                 | 5.6    | 4.8                 |
| Pb    | 0      | 0.15                | 0      | 0                   |
| Mn    | 3.4    | 2.5                 | 324    | 527                 |
| Mo    | 3.6    | 2.8                 | 19     | 32.7                |
| Se    | 5.6    | 6.6                 | 5.6    | 1.2                 |
| V     | 0      | 0                   | 0      | 0                   |
| Zn    | --     | 6.25                | --     | 4.65                |

# CONTINUOUS FLOW RELEACHING
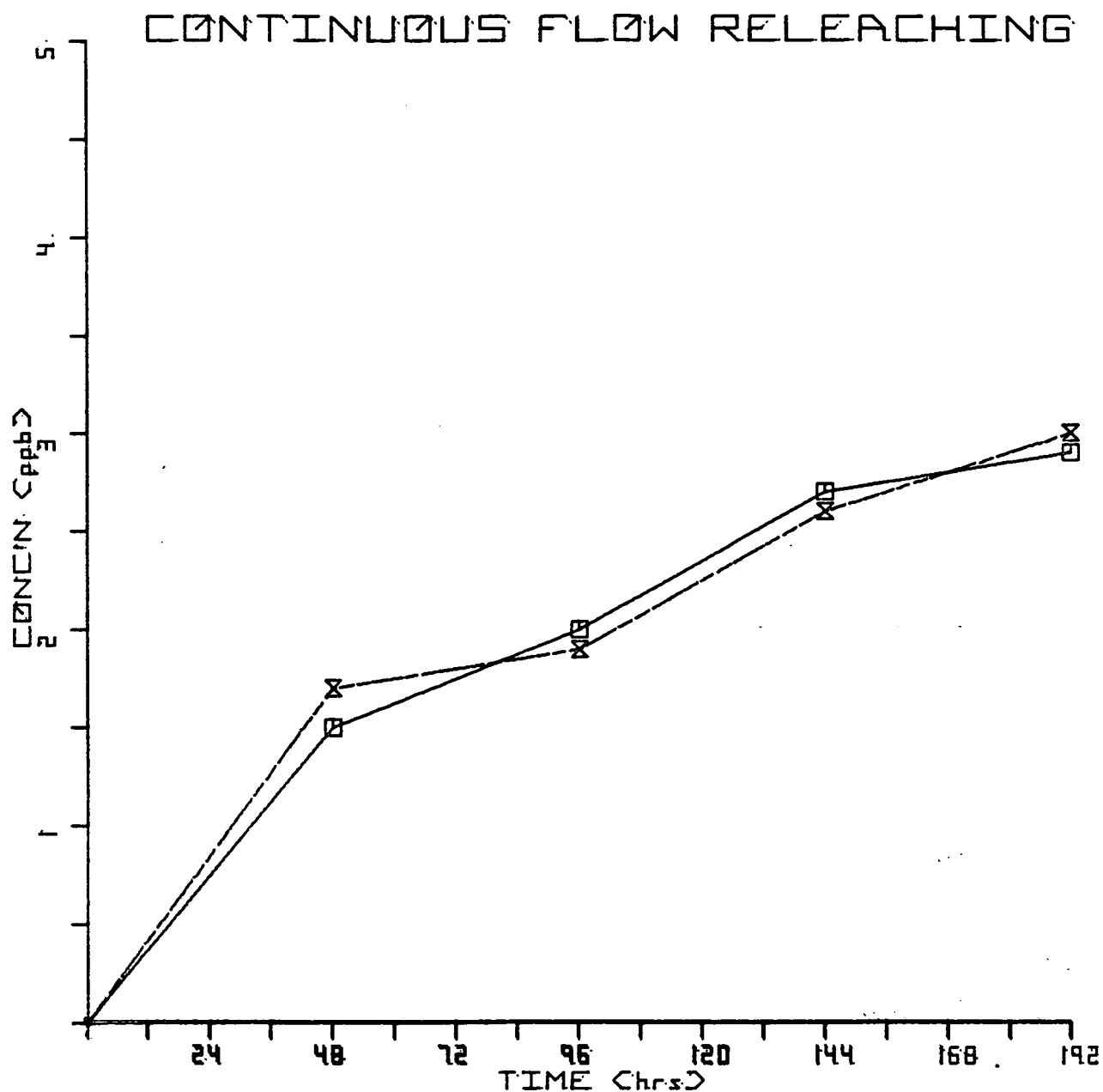


FIGURE V-D-2:     ARSENIC
                  WESTERN COAL NO. 1 (0.25-0.50 MM)
                  DEIONIZED WATER LEACHANT
                  COAL/LEACHANT RATIO = 0.2 G./1.0 G
                  AIR ATMOSPHERE
                  TOTAL RELEASE
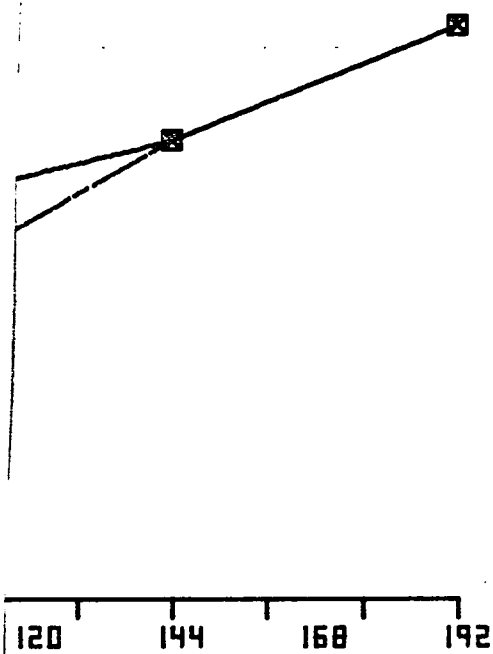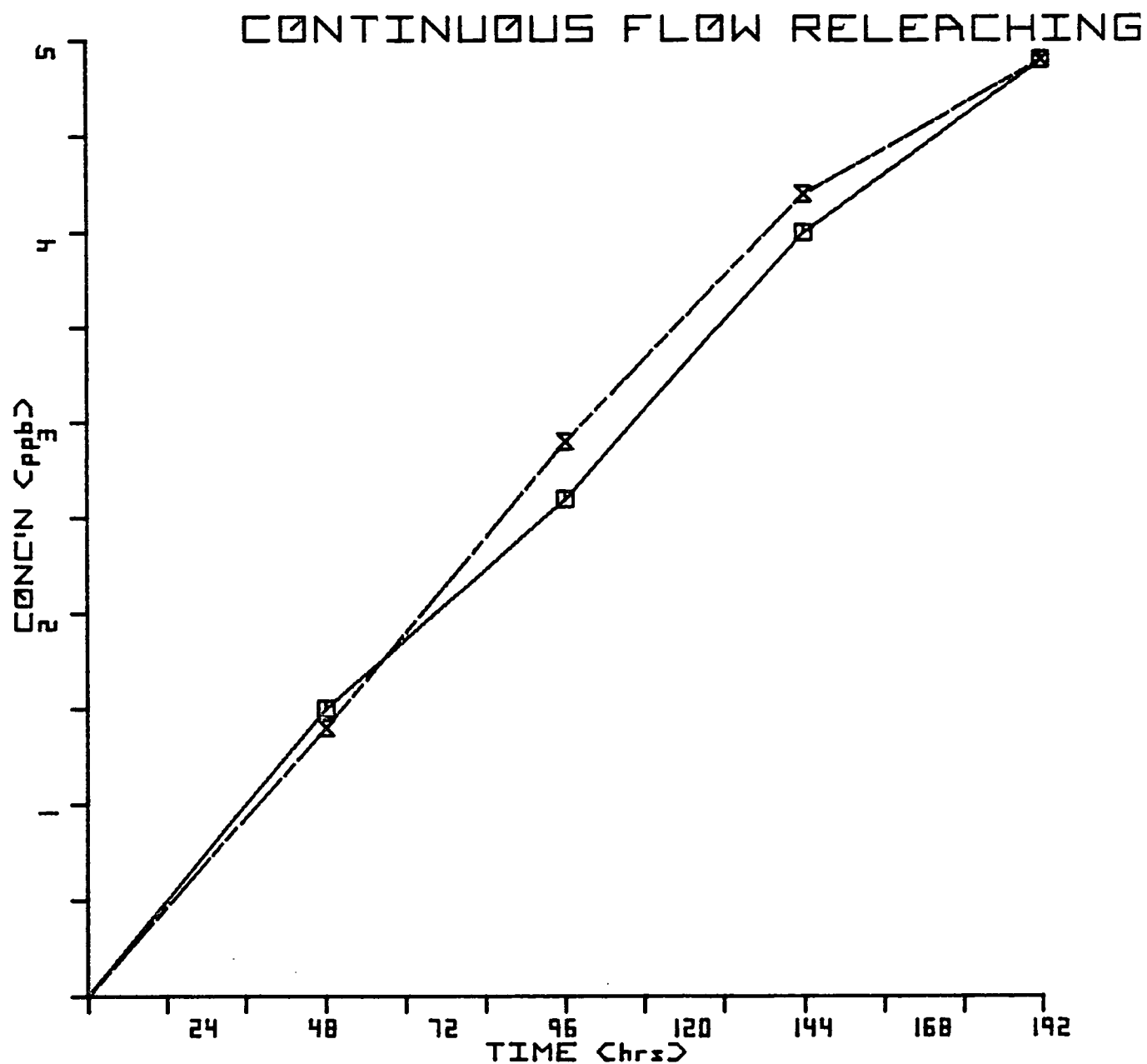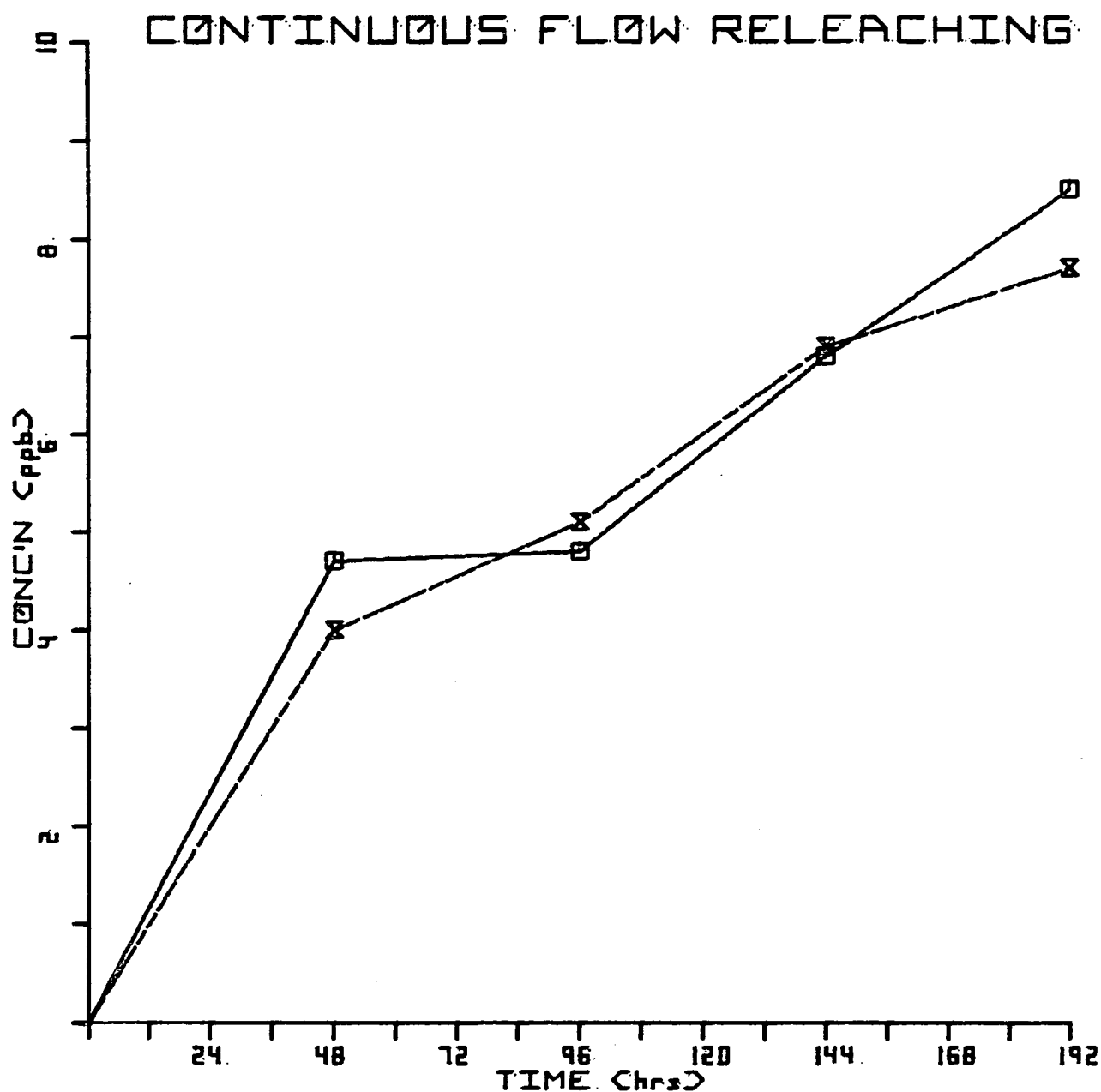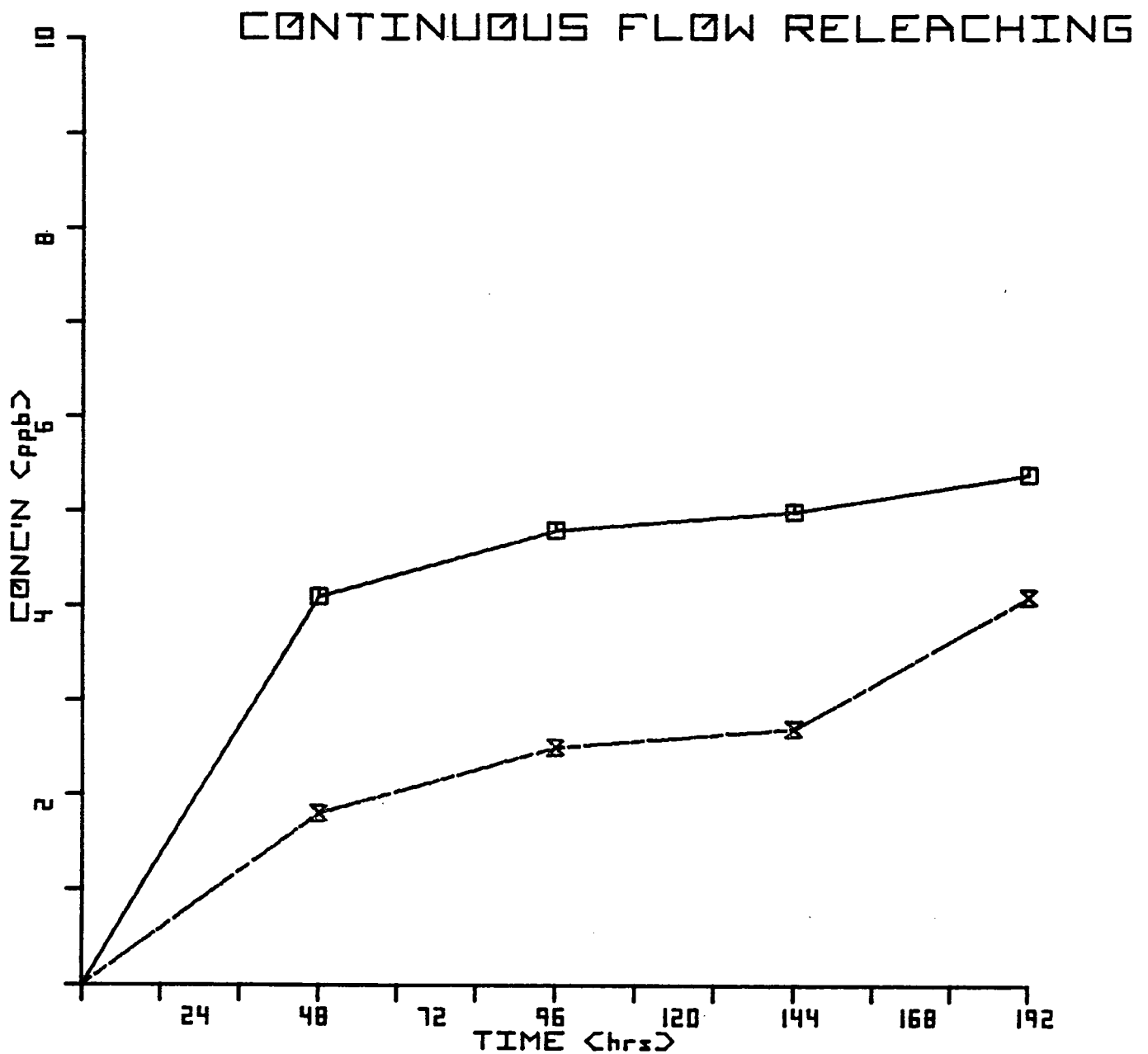                  ——⊟—— = REPLICATE NO. 1
                  ——✕—— = REPLICATE NO. 2

# CONTINUOUS FLOW RELEACHING
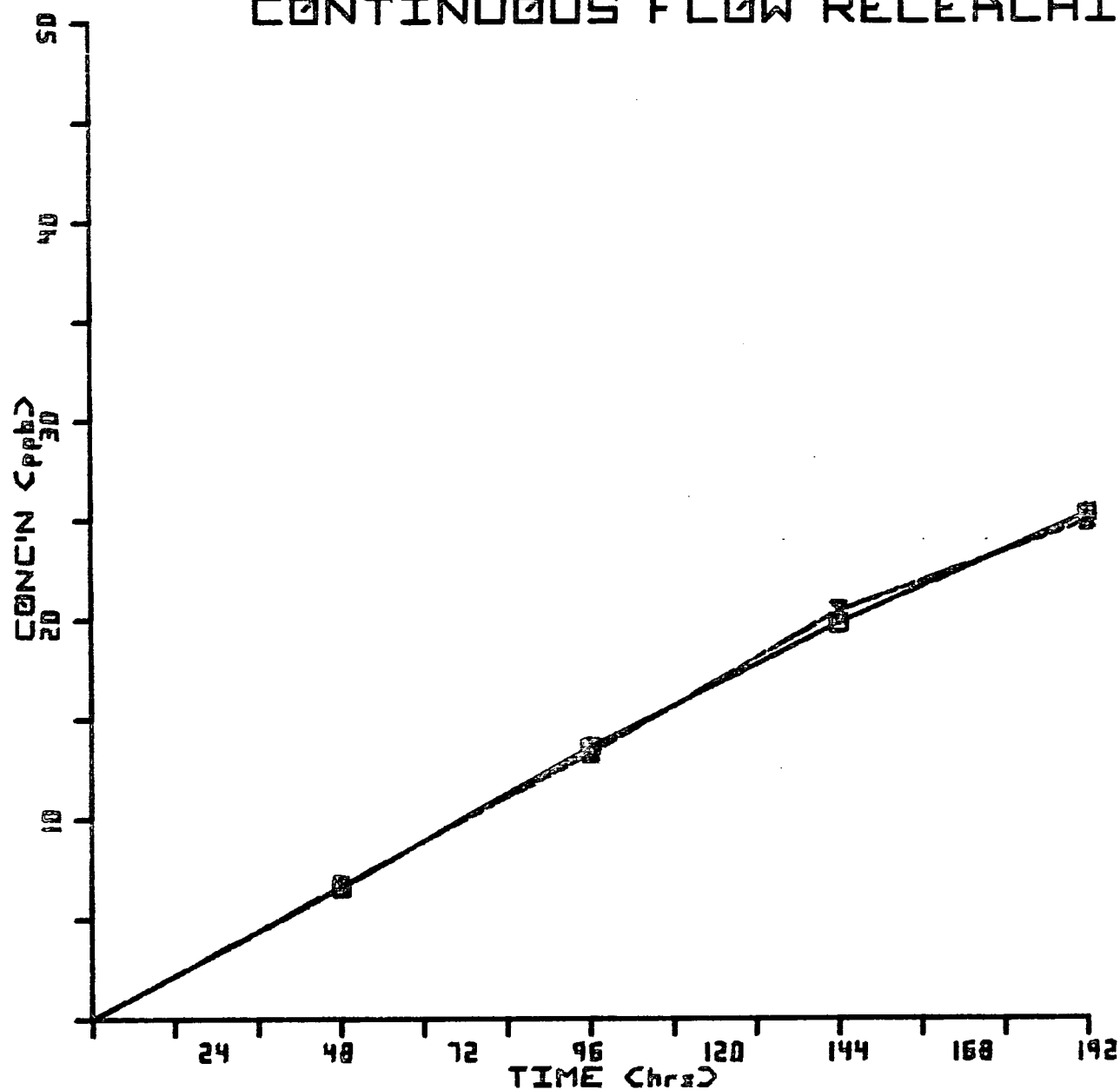


FIGURE V-D-3:     ARSENIC
WESTERN COAL NO. 1 (0.25-0.50 mm)
ACETATE BUFFER LEACHANT
COAL/LEACHANT RATIO = 0.2g./1.0g.
AIR ATMOSPHERE
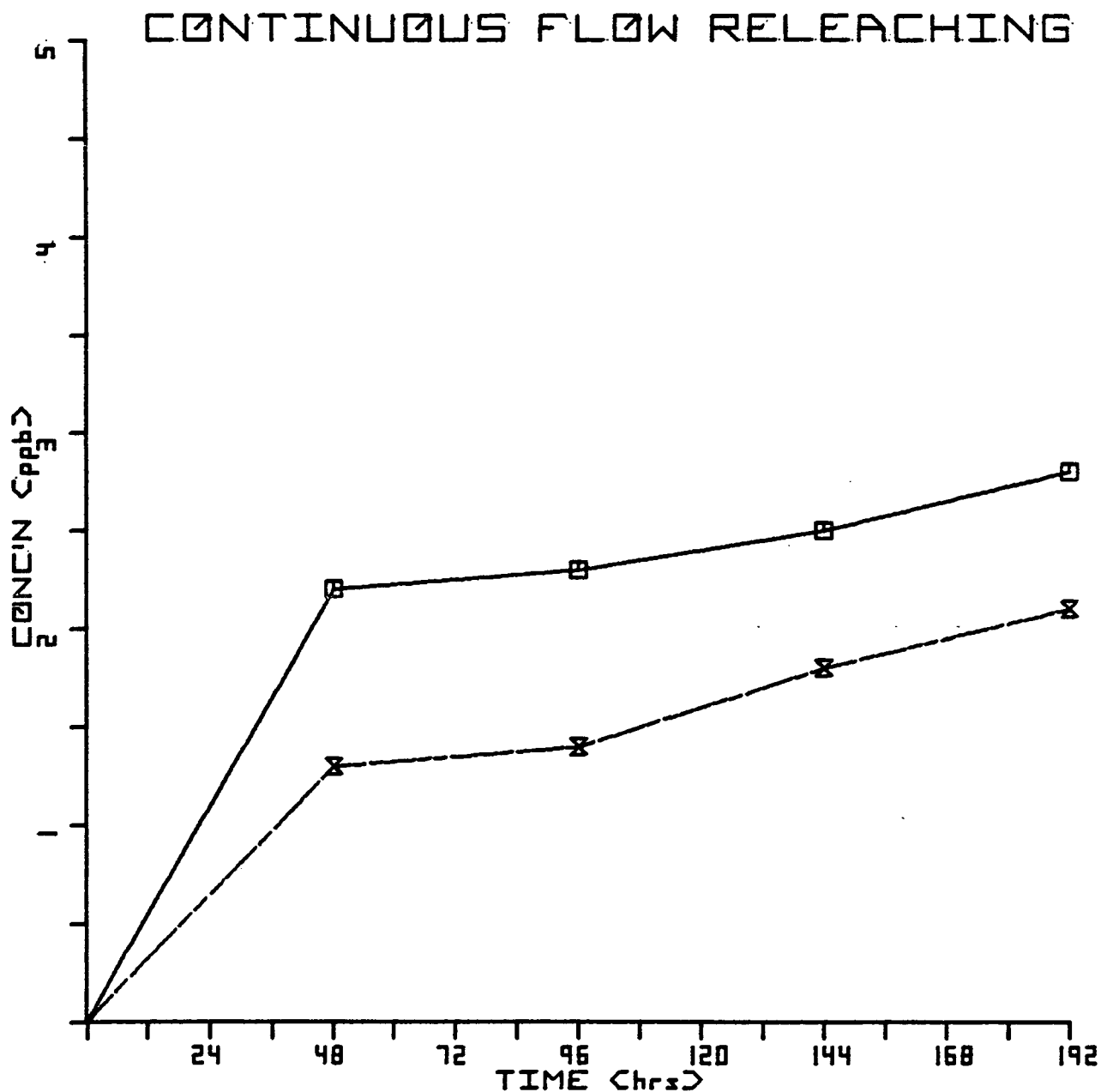TOTAL RELEASE
      = REPLICATE NO. 1
      = REPLICATE NO. 2

75
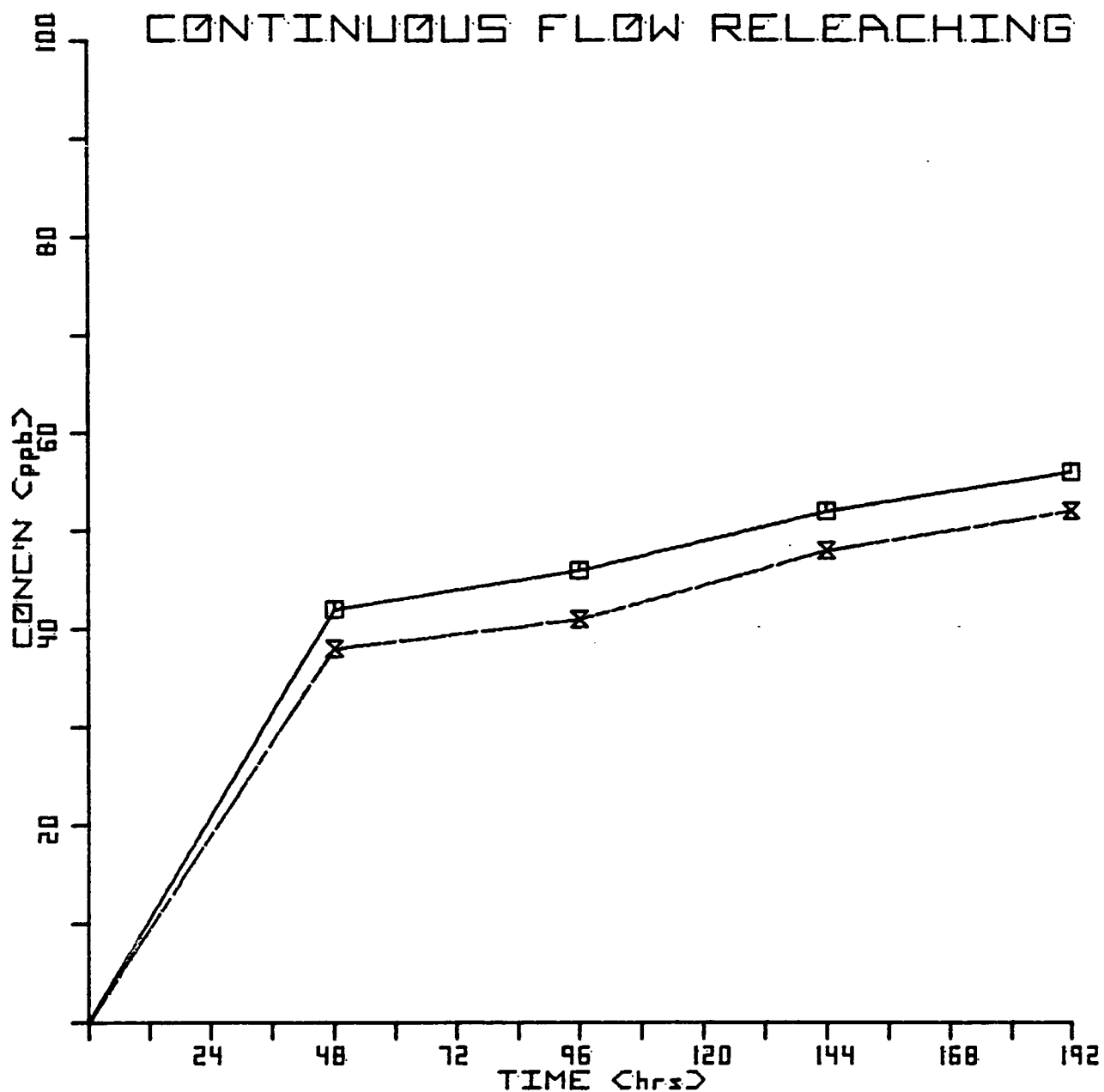
FIGURE V-D-4:    BARIUM
WESTERN COAL NO. 1 (0.25-0.50 MM)
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE
————⊟———— = REPLICATE NO. 1
————✕———— = REPLICATE NO. 2

76

# CONTINUOUS FLOW RELEACHING
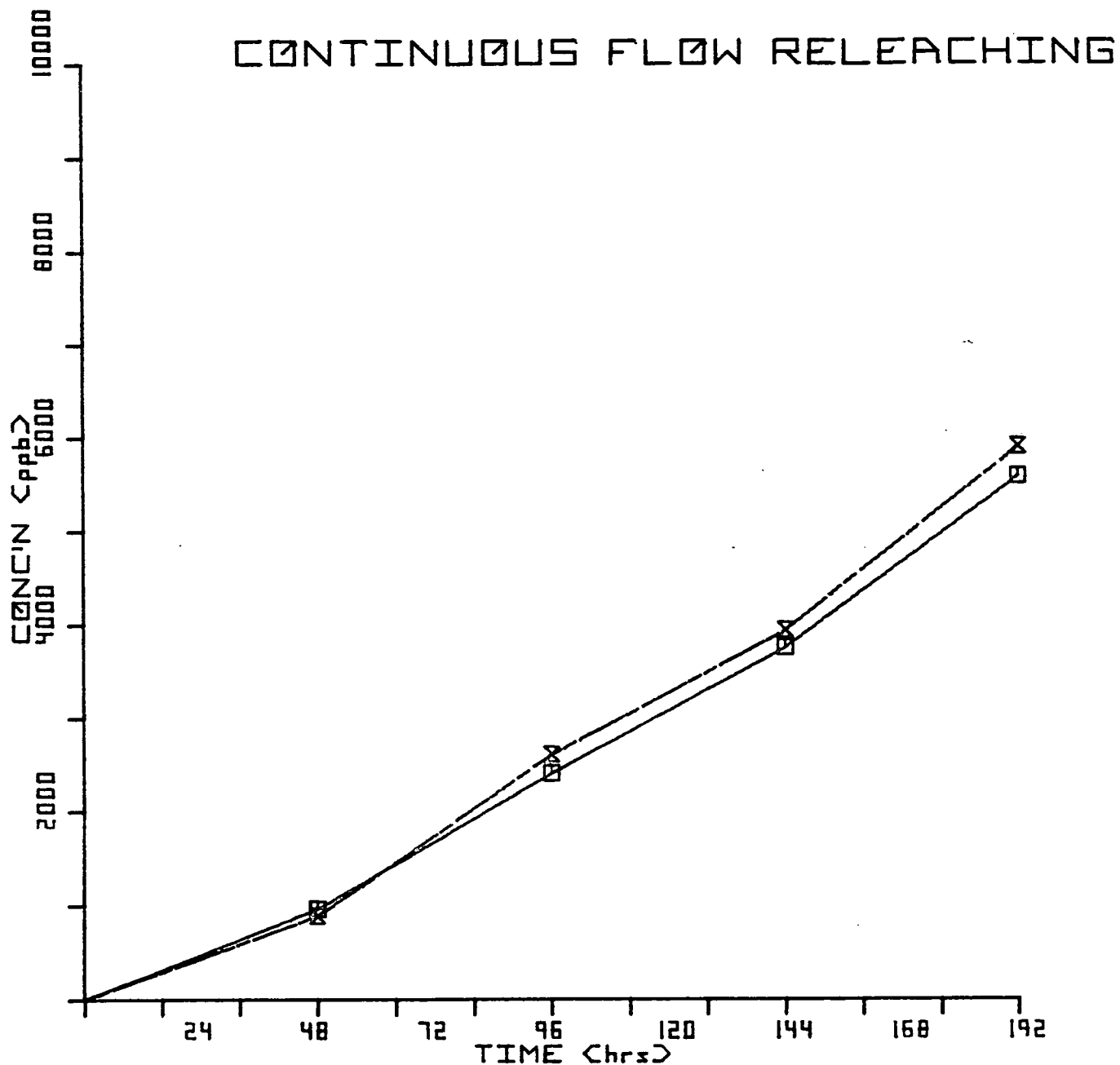
FIGURE V-D-5:    BARIUM
WESTERN COAL NO. 1 <0.25-0.50 mm>
ACETATE BUFFER LEACHANT
COAL/LEACHANT RATIO = 0.2g./1.0g.
AIR ATMOSPHERE
TOTAL RELEASE
___▣___ = REPLICATE NO. 1
___✕___ = REPLICATE NO. 2
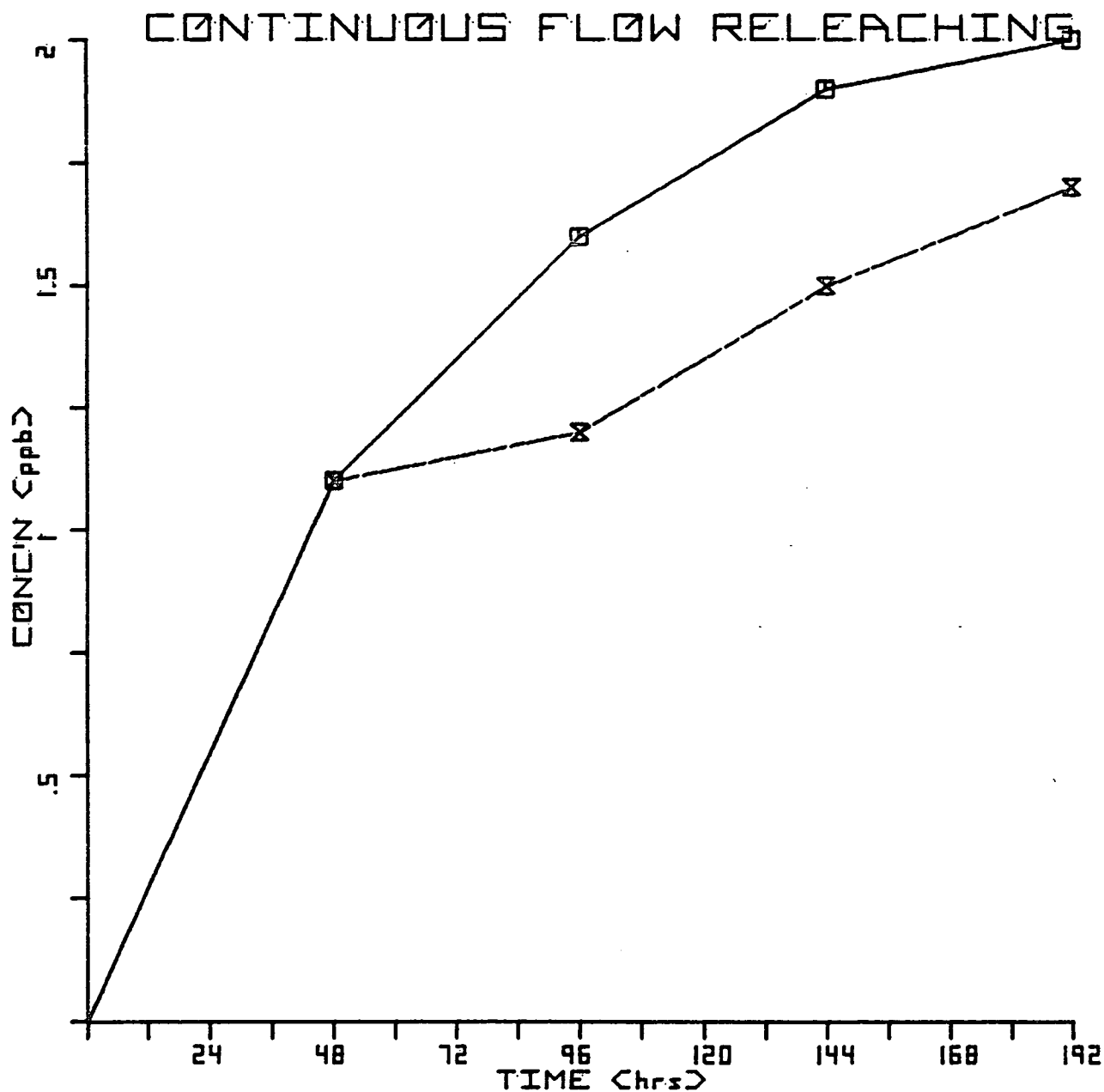
FIGURE V-D-6: CADMIUM
WESTERN COAL NO. 1 (0.25-0.50 MM)
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE
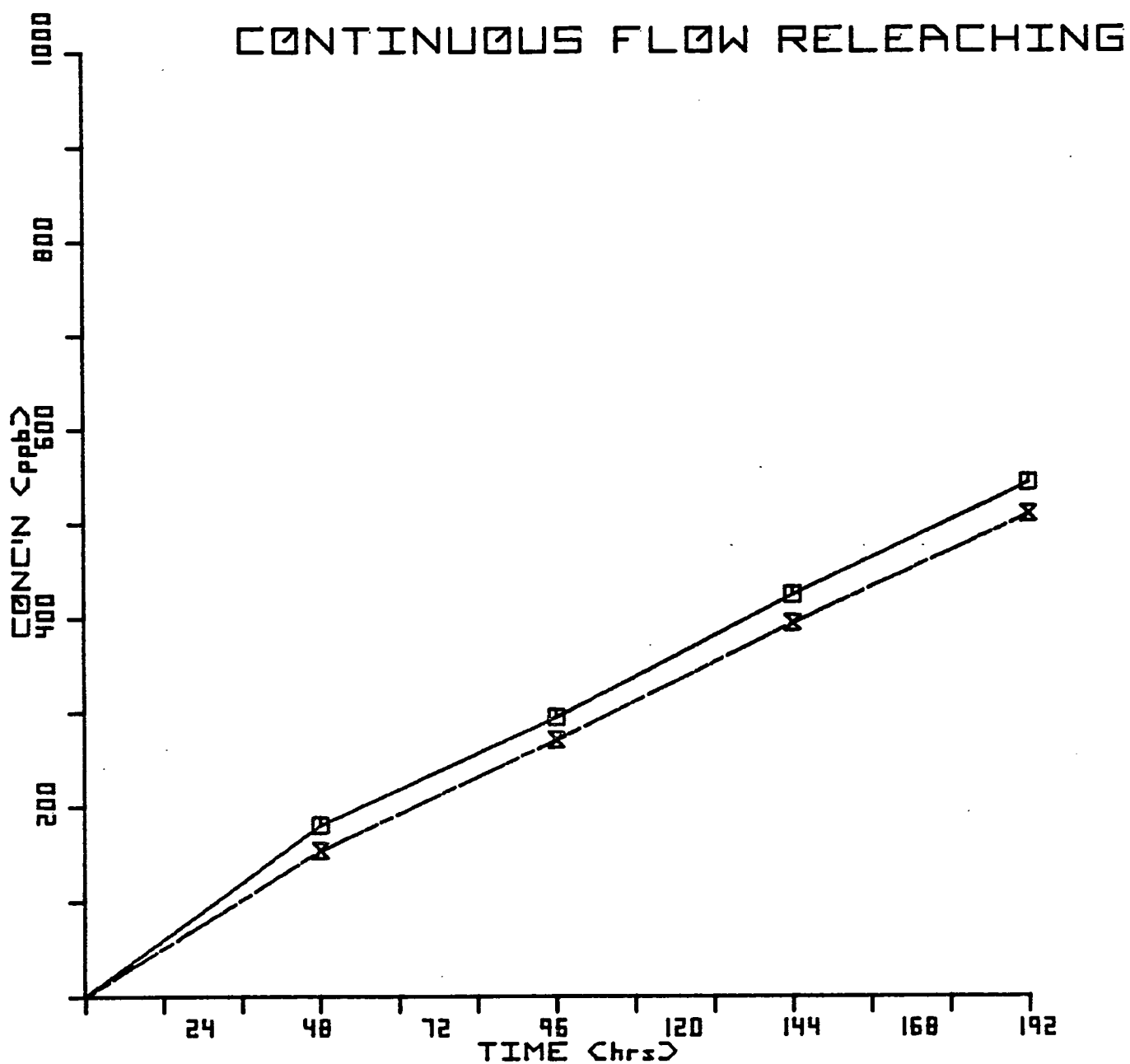———□——— = REPLICATE NO. 1
——✕—— = REPLICATE NO. 2

78

CONTINUOUS FLOW RELEACHING
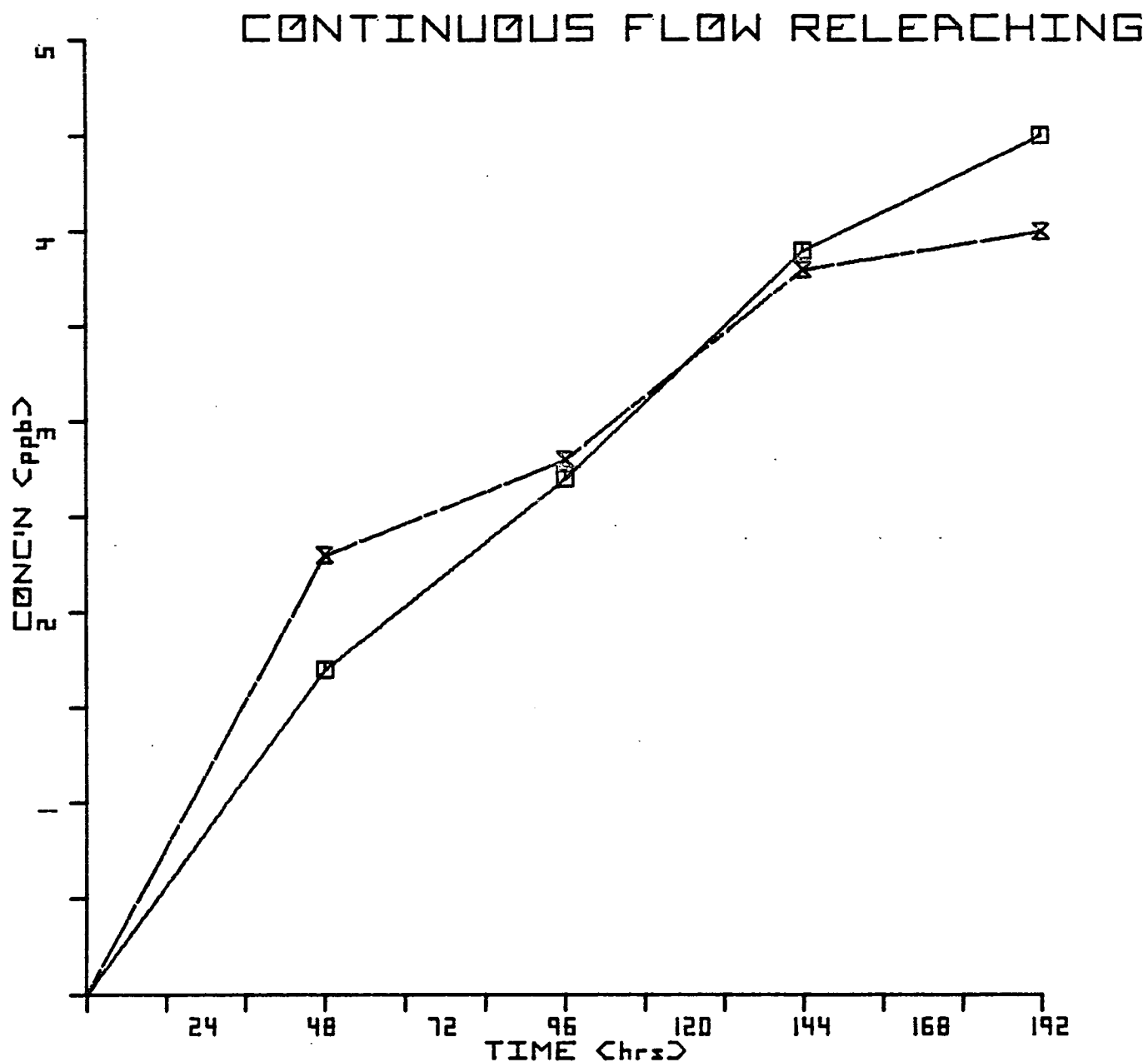
FIGURE V-D-7:  CADMIUM
WESTERN COAL NO. 1 <0.25-0.50 mm>
ACETATE BUFFER LEACHANT
COAL/LEACHANT RATIO = 0.2g./1.0g.
AIR ATMOSPHERE
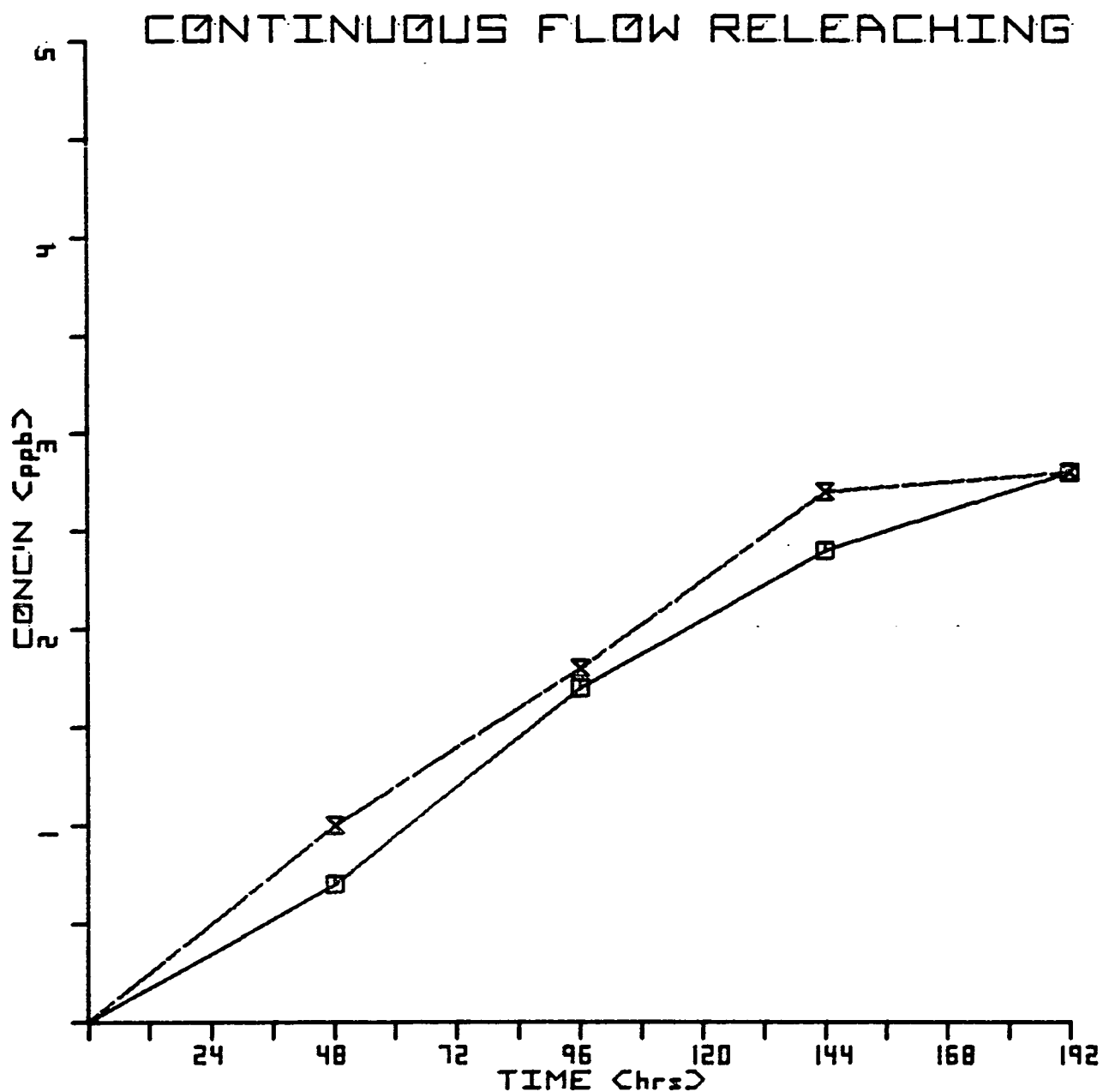TOTAL RELEASE
─□─ = REPLICATE NO. 1
─⊠─ = REPLICATE NO. 2

79
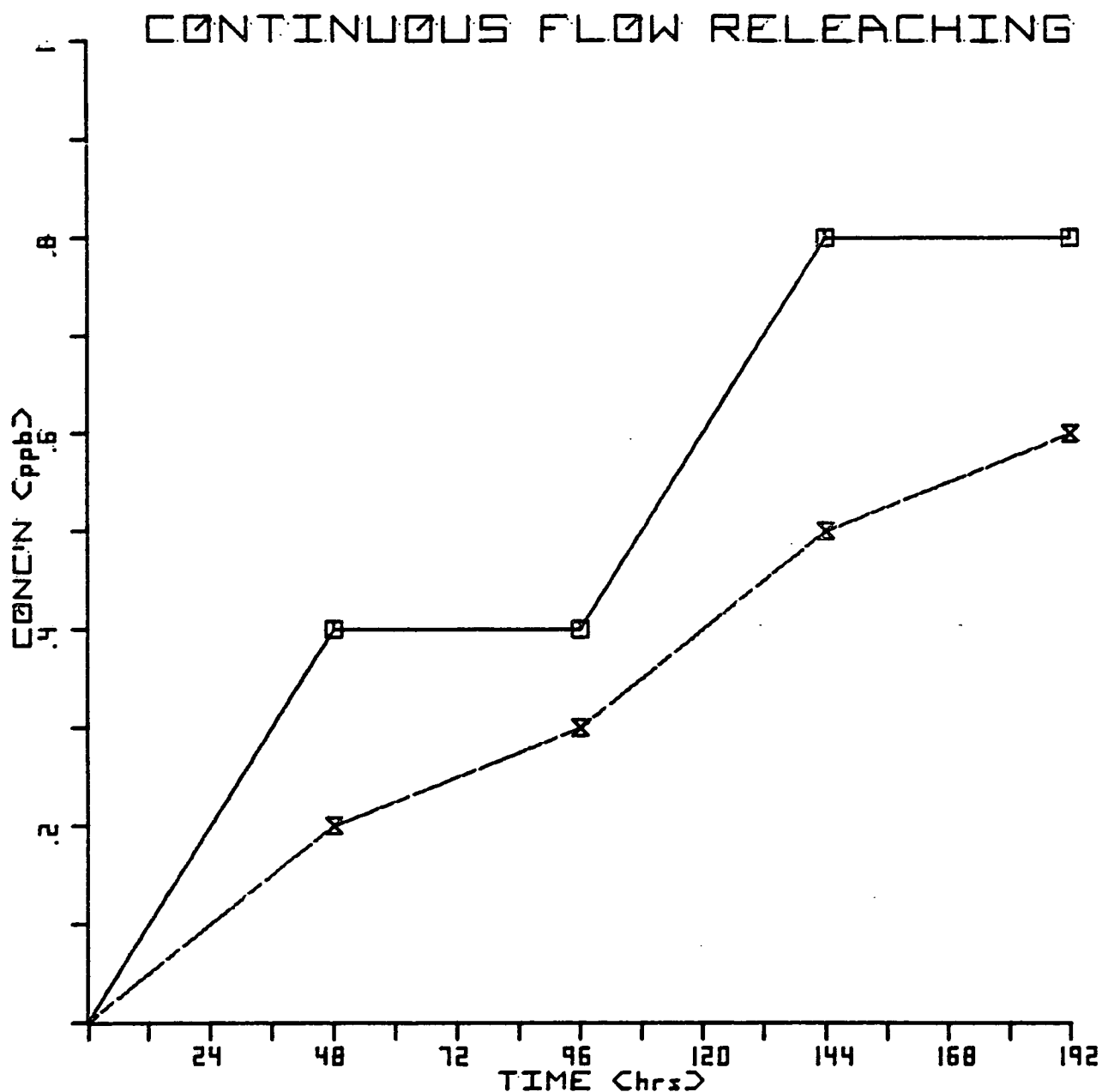
FIGURE V-D-8:     CHROMIUM
WESTERN COAL NO. 1 (0.25-0.50 MM)
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE
———□——— = REPLICATE NO. 1
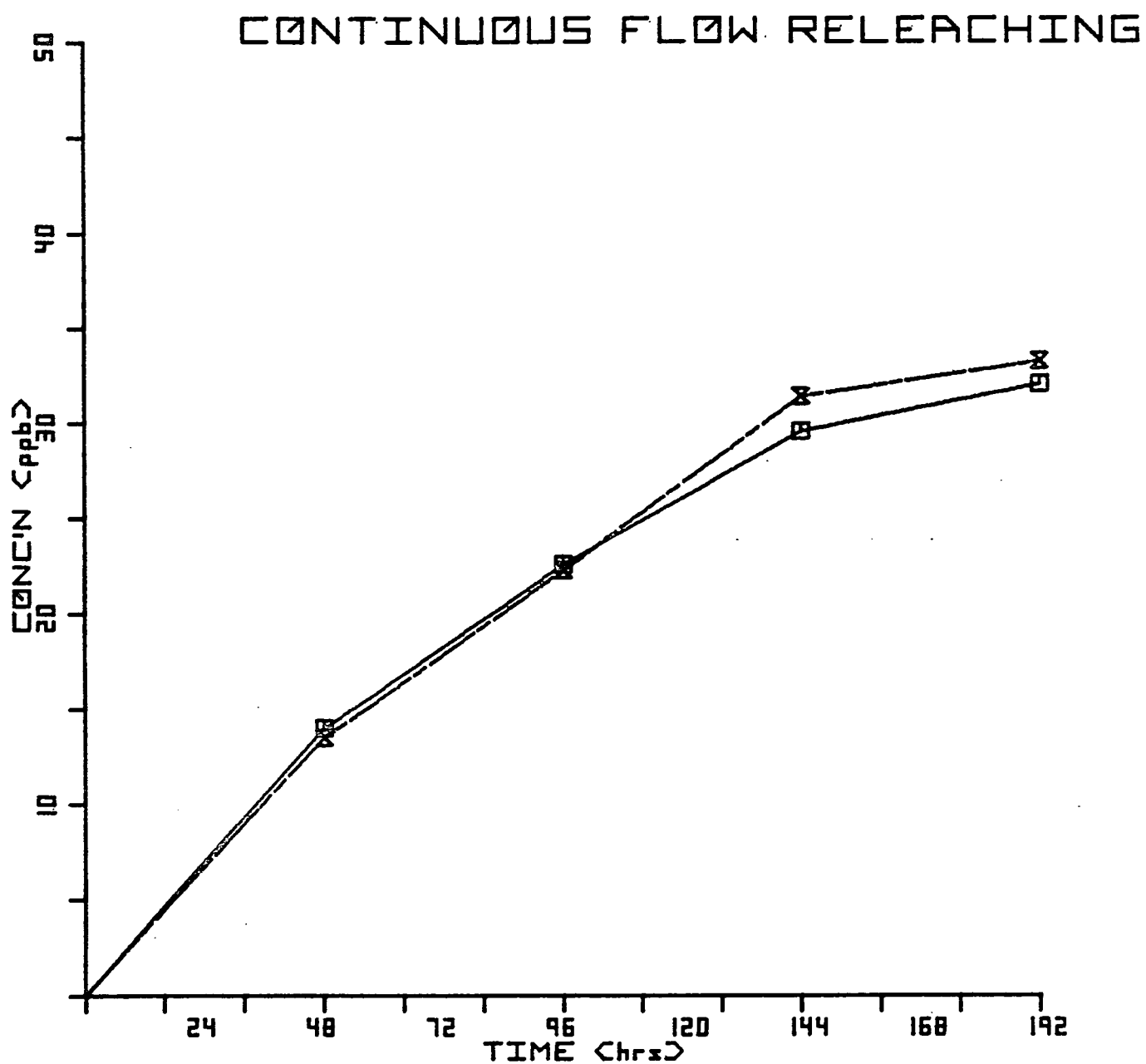——–X—–– = REPLICATE NO. 2

# CONTINUOUS FLOW RELEACHING
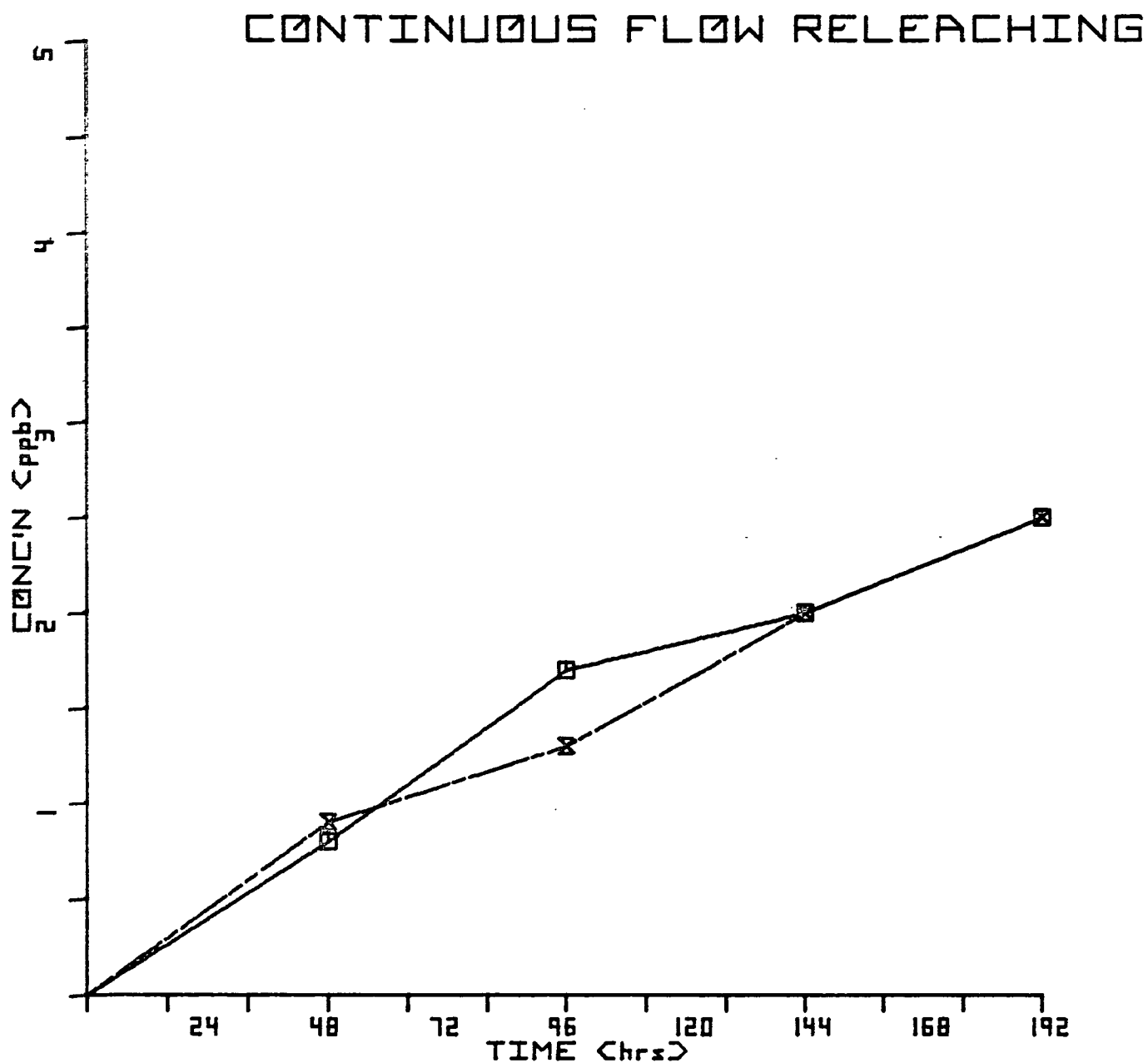


FIGURE V-D-9:     CHROMIUM
WESTERN COAL NO. 1 (0.25-0.50 mm)
ACETATE BUFFER LEACHANT
COAL/LEACHANT RATIO = 0.2g./1.0g.
AIR ATMOSPHERE
TOTAL RELEASE
——☐—— = REPLICATE NO. 1
—·—☒—·— = REPLICATE NO. 2

# J0US FL0W RELEACHING

TIME (hrs)
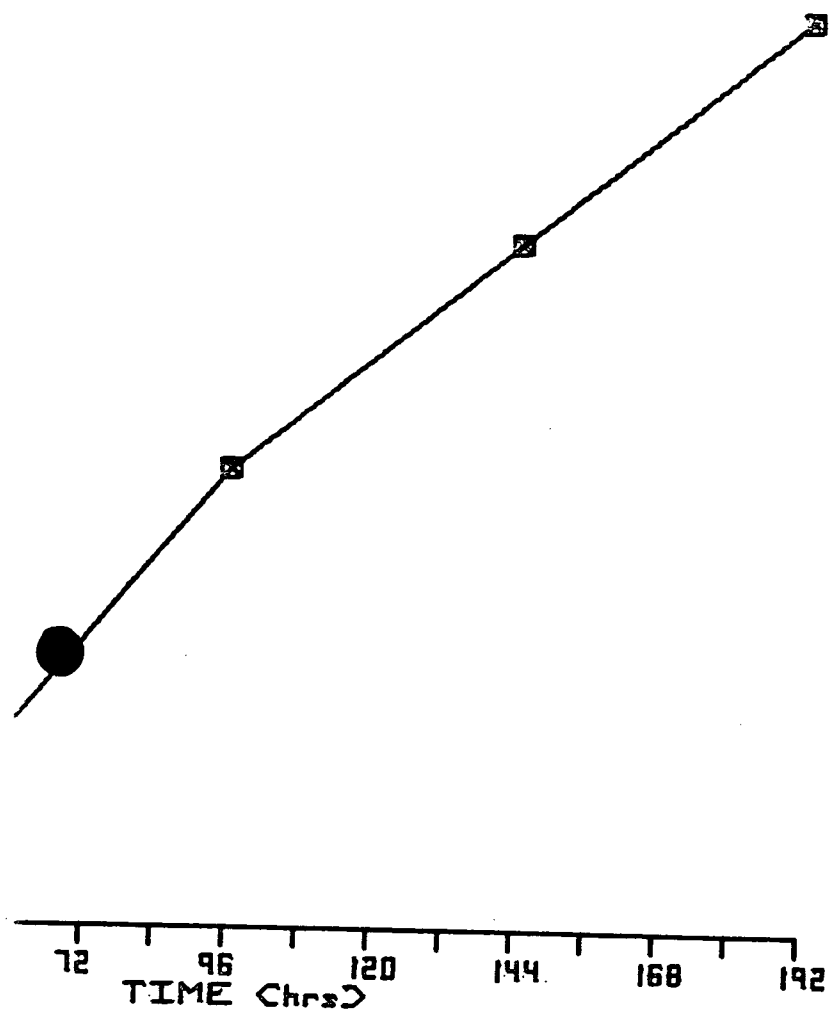
ALT
TERN COAL NO. 1 (0.25-0.50 MM)
0NIZED WATER LEACHANT
L/LEACHANT RATIO = 0.2 G./1.0 G
 ATMOSPHERE
AL RELEASE
. = REPLICATE NO. 1
. = REPLICATE NO. 2

. 1 (0.25-0.50 mm)
LEACHANT
RATIO = 0.2g./1.0g.

E NO. 1
E NO. 2

82

FIGURE V-D-11:   COBALT
WESTERN COAL NO. 1 <0.25-0.50 mm>
ACETATE BUFFER LEACHANT
COAL/LEACHANT RATIO = 0.2g./1.0g.
AIR ATMOSPHERE
TOTAL RELEASE
____▣____ = REPLICATE NO. 1
__-__≍__-__ = REPLICATE NO. 2

83

# CONTINUOUS FLOW RELEACHING



FIGURE V-D-12:     COPPER
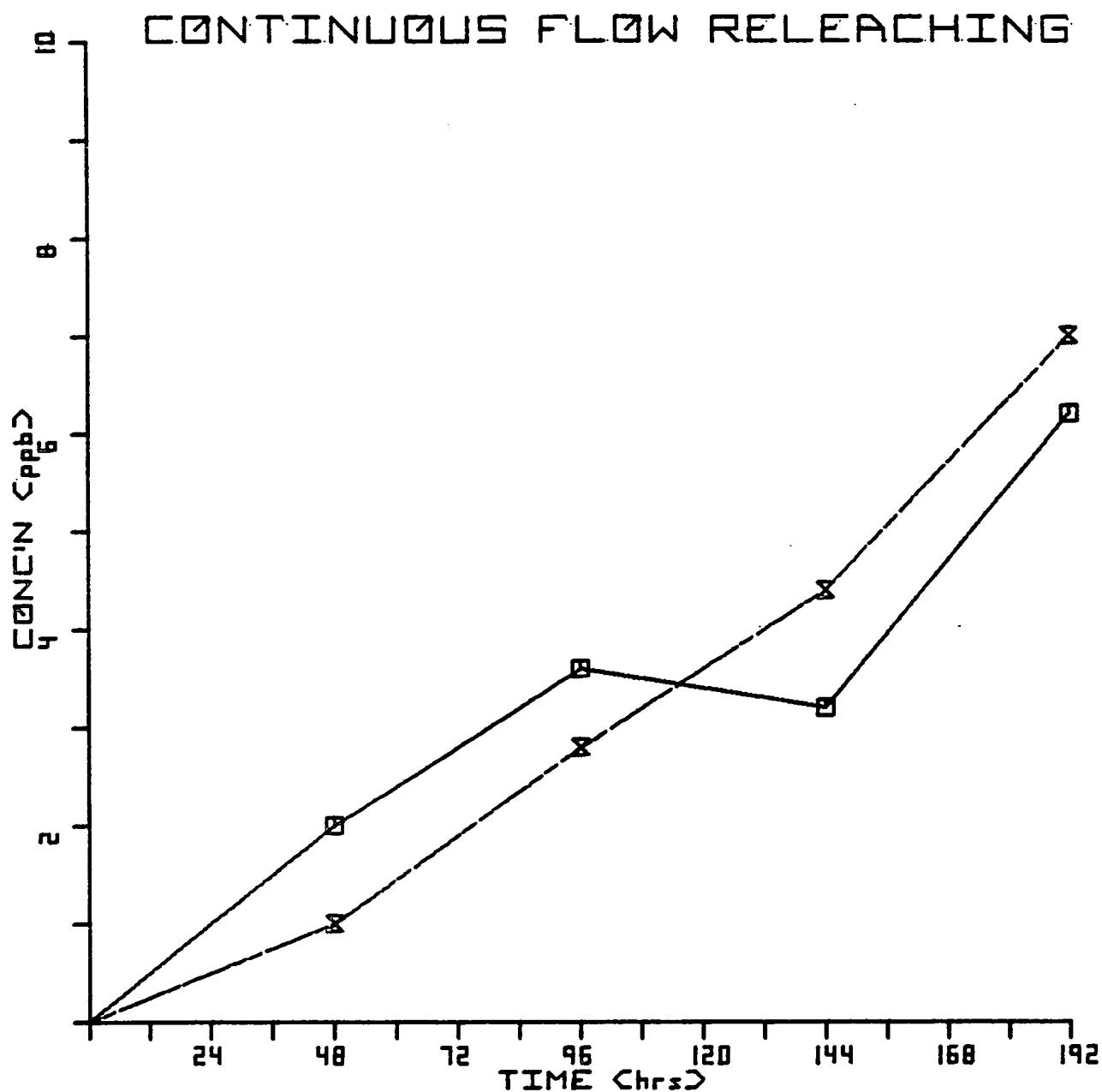                             WESTERN COAL NO. 1 (0.25-0.50 MM)
                             DEIONIZED WATER LEACHANT
                             COAL/LEACHANT RATIO : 0.2 G./1.0 G
                             AIR ATMOSPHERE
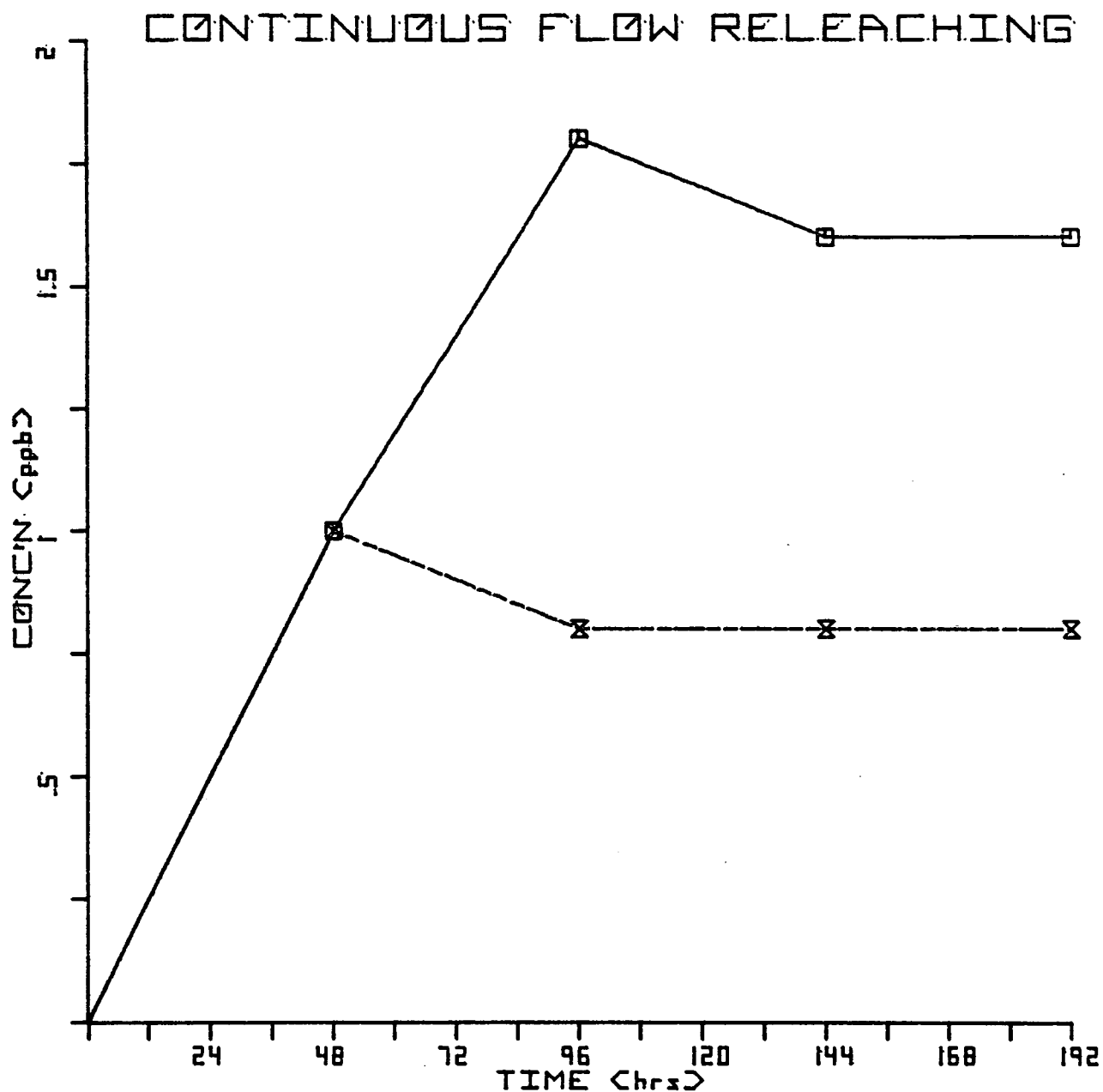                             TOTAL RELEASE
                             ———□—— : REPLICATE NO. 1
                             ——✕—— : REPLICATE NO. 2

# CONTINUOUS FLOW RELEACHING



FIGURE V-D-13:    COPPER
WESTERN COAL NO. 1 (0.25-0.50 mm)
ACETATE BUFFER LEACHANT
COAL/LEACHANT RATIO = 0.2g./1.0g.
AIR ATMOSPHERE
TOTAL RELEASE
——▣—— = REPLICATE NO. 1
——✕——. = REPLICATE NO. 2

CONTINUOUS FLOW RELEACHING

FIGURE V-D-14:    MANGANESE
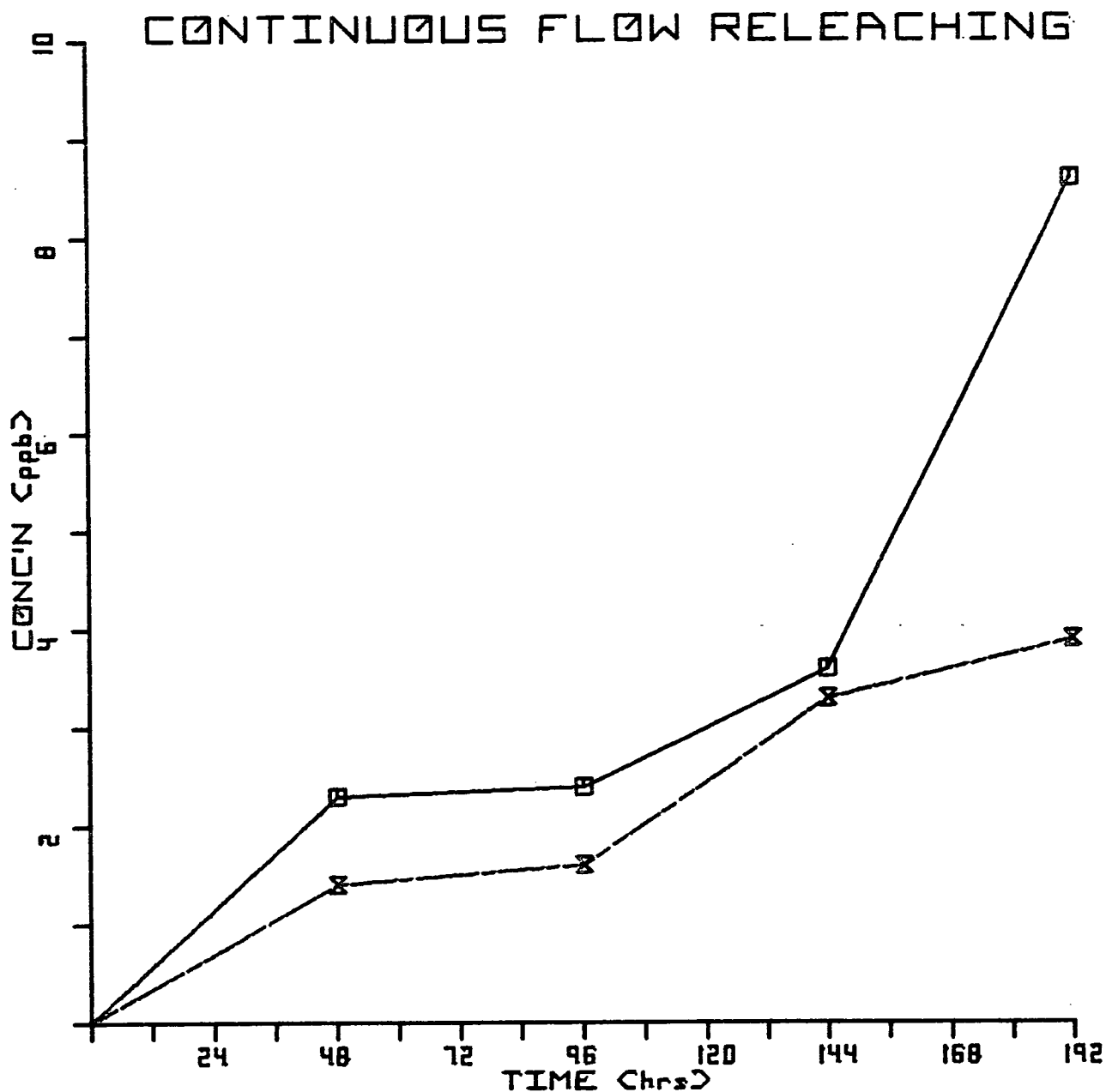                 WESTERN COAL NO. 1 (0.25-0.50 MM)
                 DEIONIZED WATER LEACHANT
                 COAL/LEACHANT RATIO = 0.2 G./1.0 G
                 AIR ATMOSPHERE
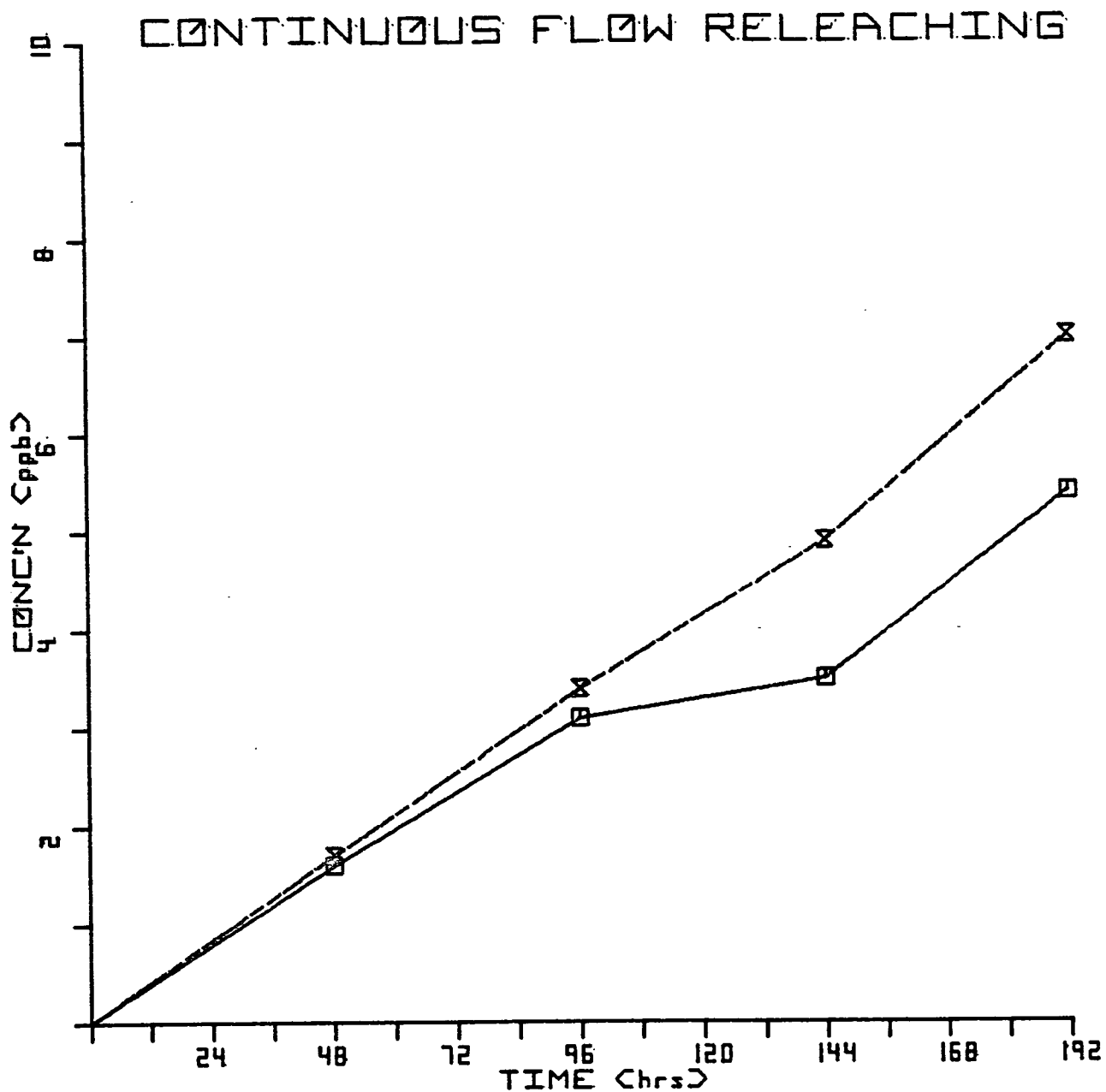                 TOTAL RELEASE
                 ──▣── = REPLICATE NO. 1
                 ──☒── = REPLICATE NO. 2

FIGURE V-D-15: MANGANESE
WESTERN COAL NO. 1 <0.25-0.50 mm>
ACETATE BUFFER LEACHANT
COAL/LEACHANT RATIO = 0.2g./1.0g.
AIR ATMOSPHERE
TOTAL RELEASE
—☐— = REPLICATE NO. 1
—✗— = REPLICATE NO. 2

87

CONTINUOUS FLOW RELEACHING

FIGURE V-D-16:   MOLYBDENUM
WESTERN COAL NO. 1 <0.25-0.50 MM>
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE
━━▣━━ = REPLICATE NO. 1
━━☒━━ = REPLICATE NO. 2

FIGURE V-D-17: MOLYBDENUM
WESTERN COAL NO. 1 (0.25-0.50 mm)
ACETATE BUFFER LEACHANT
COAL/LEACHANT RATIO = 0.2g./1.0g.
AIR ATMOSPHERE
TOTAL RELEASE
⊡ = REPLICATE NO. 1
△ = REPLICATE NO. 2

89

CONTINUOUS FLOW RELEACHING

FIGURE V-D-18:    SELENIUM
WESTERN COAL NO. 1 (0.25-0.50 MM)
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE
———⊡——— = REPLICATE NO. 1
—·—·⊠·—·— = REPLICATE NO. 2

90

FIGURE V-D-19: SELENIUM
WESTERN COAL NO. 1 <0.25-0.50 MM>
ACETATE BUFFER LEACHANT
COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE
───▣─── = REPLICATE NO. 1
──·─✕·── = REPLICATE NO. 2

91

FIGURE V-D-20: ZINC
WESTERN COAL NO. 1 (0.25-0.50 MM)
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE
▭ = REPLICATE NO. 1
✕ = REPLICATE NO. 2

92

FIGURE V-D-21:  ZINC
WESTERN COAL NO. 1 (0.25-0.50 MM)
ACETATE BUFFER LEACHANT
COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE
— □ — = REPLICATE NO. 1
— X — = REPLICATE NO. 2

93

## 3. Releaching Shaker Runs

### a. Experimental--

The purpose of the releaching shaker runs was to determine how much additional metal could be removed from the coal by the use of additional passes of deionized water leachant.

Two 100 ml Teflon® bottles were charged with 100 gram portions of 0.250-0.500 mm sized Western Coal No. 1. Deionized water (500 ml) was added to one bottle, and 500 ml of acetate buffer was added to the other coal sample.

The two bottles were placed in a heated shaker bath, which was maintained at 40°C for the duration of the run. Shaking rate was 45 cycles per minute, with a travel of 28 mm by the shaker sample tray. Samples were collected at 48, 96, 144, 192 and 288 hours respectively.

At the time of sampling, 400 ml of each leachant was removed and the same volume of the appropriate fresh leachant was added to the bottles. This volume represented an 80 percent replacement of leachant volume at each sampling time.

The pH of the leachates were determined at the time of sampling, and then filtered through a 0.45 micron membrane filter. The filtered samples were acidified with ultrapure nitric acid to stabilize them for storage, and the metals were determined by flameless atomic absorption spectrophotometry.[1,2, 11, 15, 16] All metals except mercury were determined.

### b. Results and Discussion--

Total release values versus time are plotted in Figs. V-D-22 through V-D-39. For each metal, the deionized water leaching graph is followed by the graph for the acetate buffer leaching.

The nickel samples were lost to analysis because of nickel contamination. The zinc values appeared to be very badly contaminated and are not reported. Lead and vanadium values were zero throughout and not plotted.

The salient features of these results are: (1) metal continues to be removed from the coal with repeated releachings (except perhaps for selenium), (2) greater amounts of metal are leached by the low pH (acetate buffer) leachant (except for chromium and selenium).

These results, as well as the results of the EDTA study, the releaching factorial, the spiked runs and the continuous flow releaching, appear to show that leaching is an equilibrium controlled phenomenon with the metals being bound to the coal and yet still mobile with respect to an aqueous phase.

The generally strong agreement of these data with the data on releaching in the continuous flow system is extremely important. Shaker studies have long been used for coal leaching work, but there seemed to be some doubt that such quick and easy experiments would give results analogous to a continuous flow system. It would seem that this work would place shaker studies on a firmer foundation.
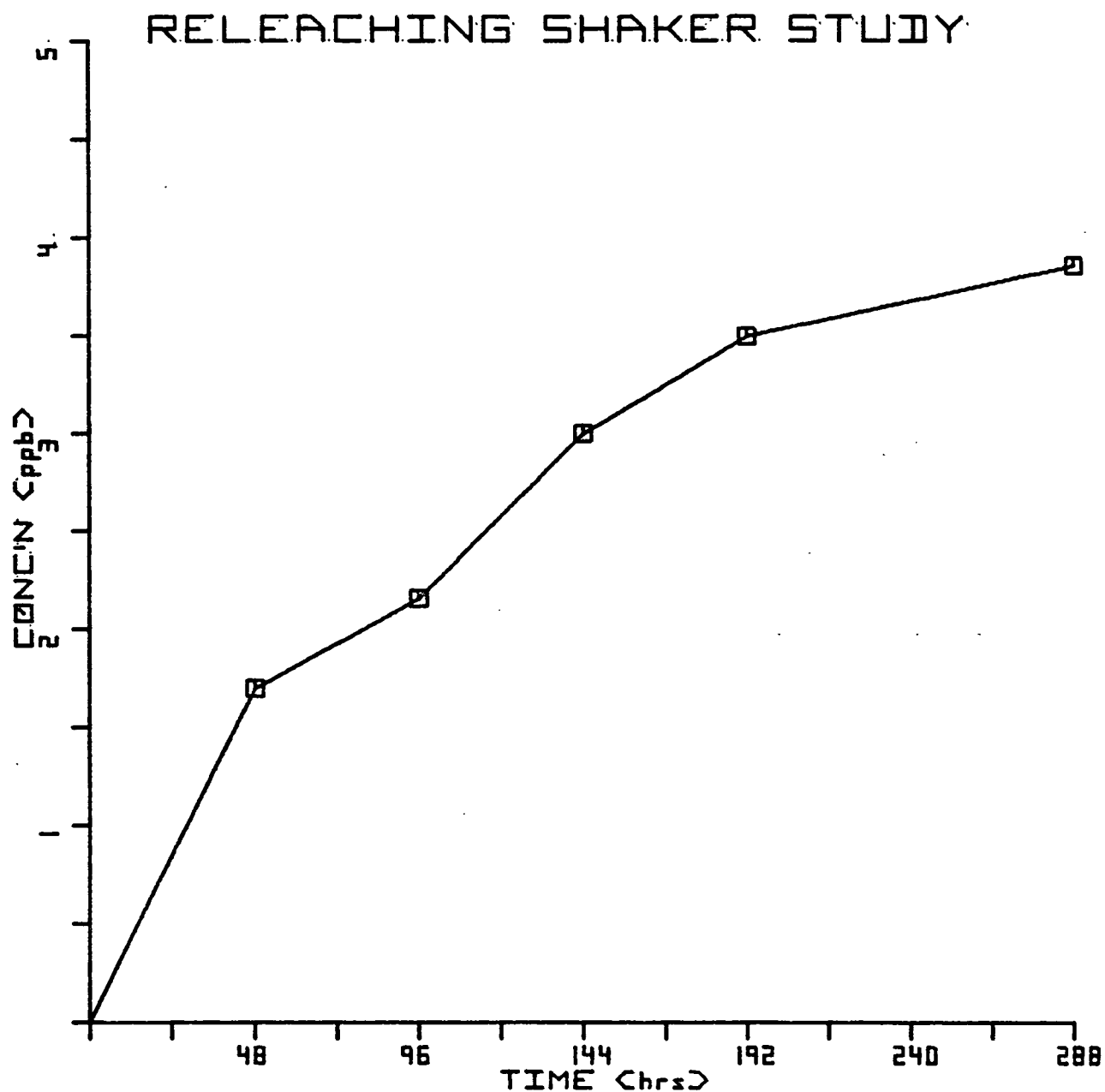
FIGURE V-D-22: ARSENIC
WESTERN COAL NO. 1 <0.25-0.50 MM>
DEIONIZED WATER LEACHANT
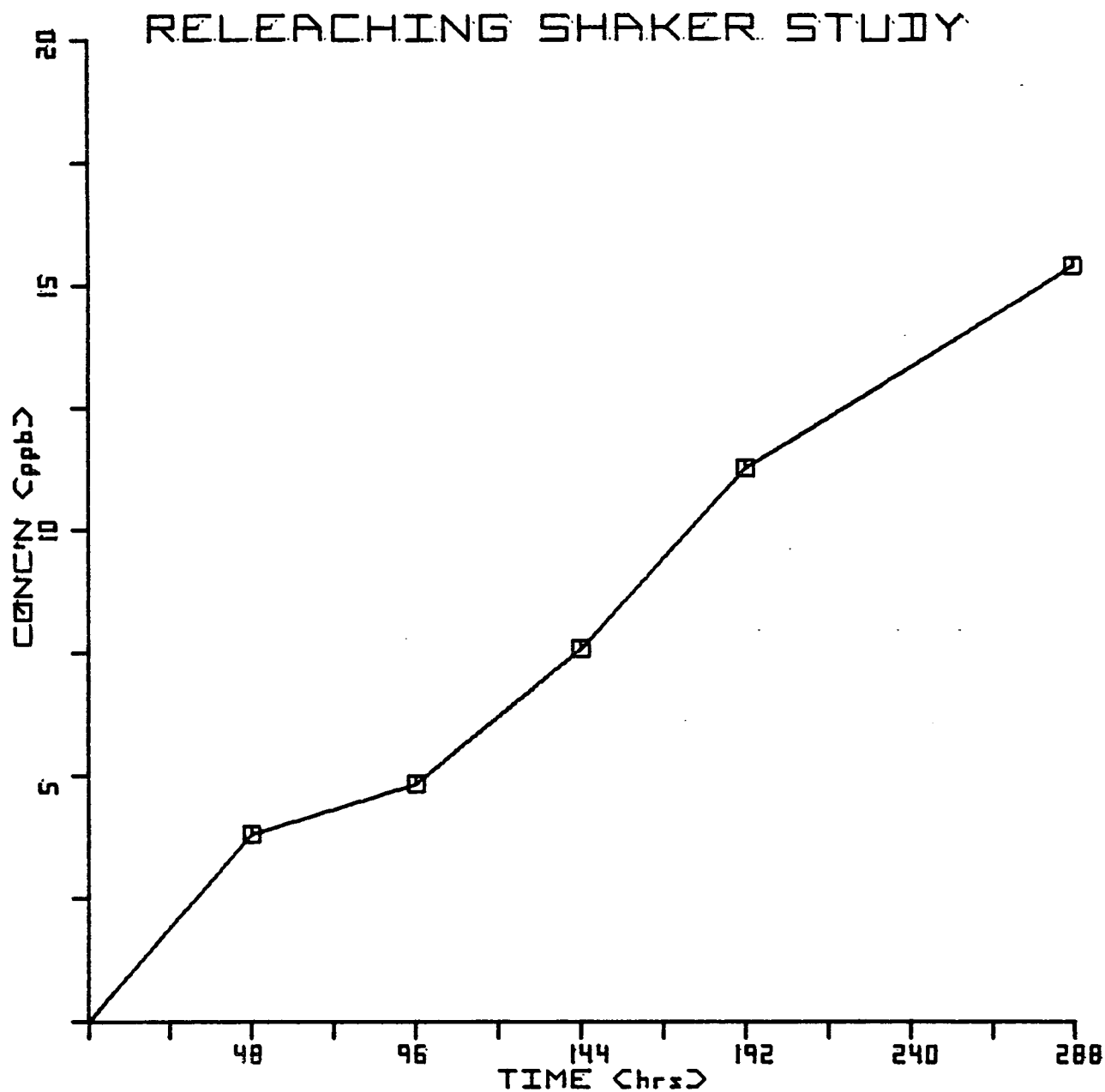COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE

FIGURE V-D-23:  ARSENIC
WESTERN COAL NO. 1 (0.25-0.50 MM)
ACETATE BUFFER LEACHANT
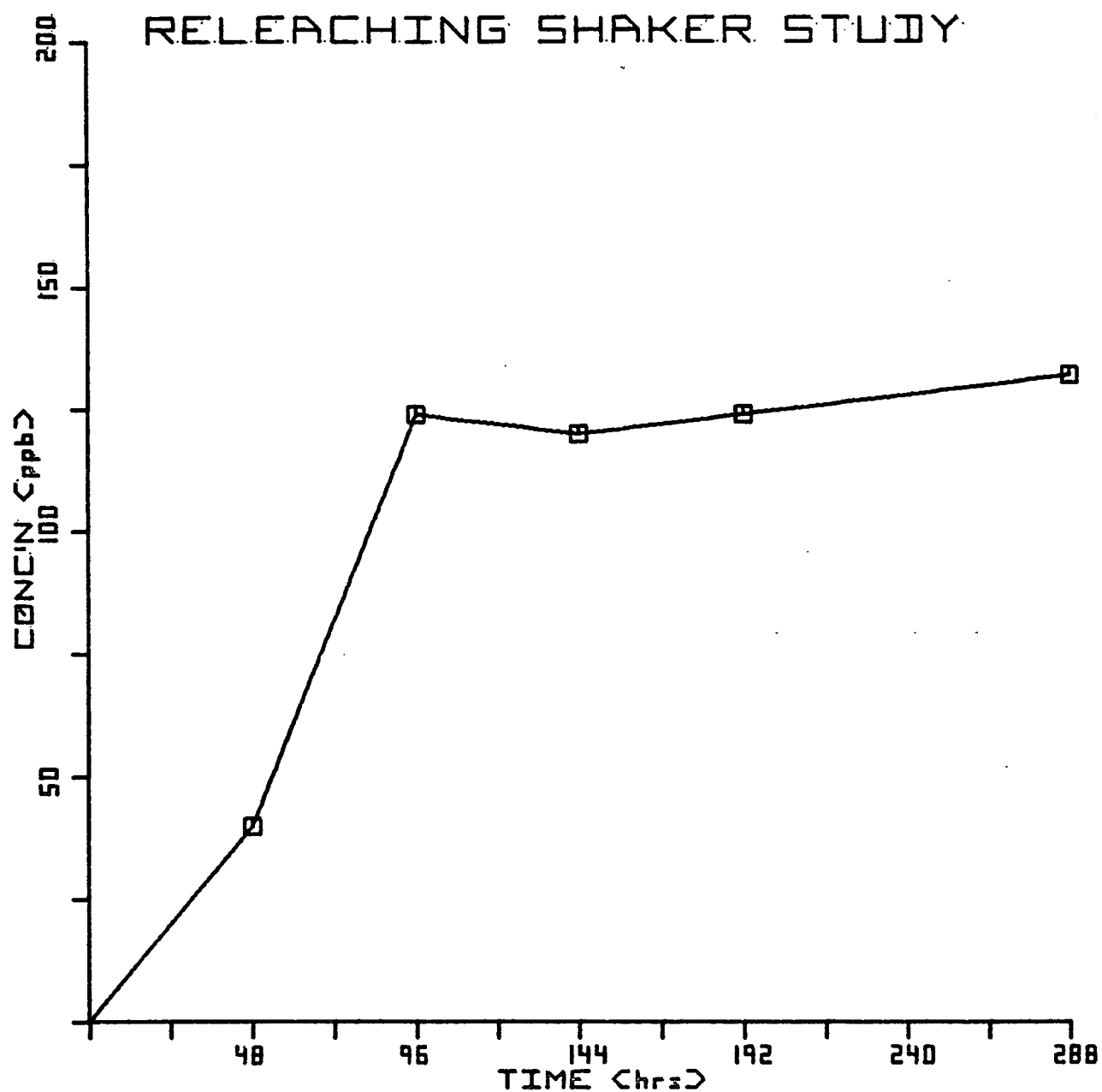COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE

FIGURE V-D-24: BARIUM
WESTERN COAL NO. 1 (0.25-0.50 MM)
DEIONIZED WATER LEACHANT
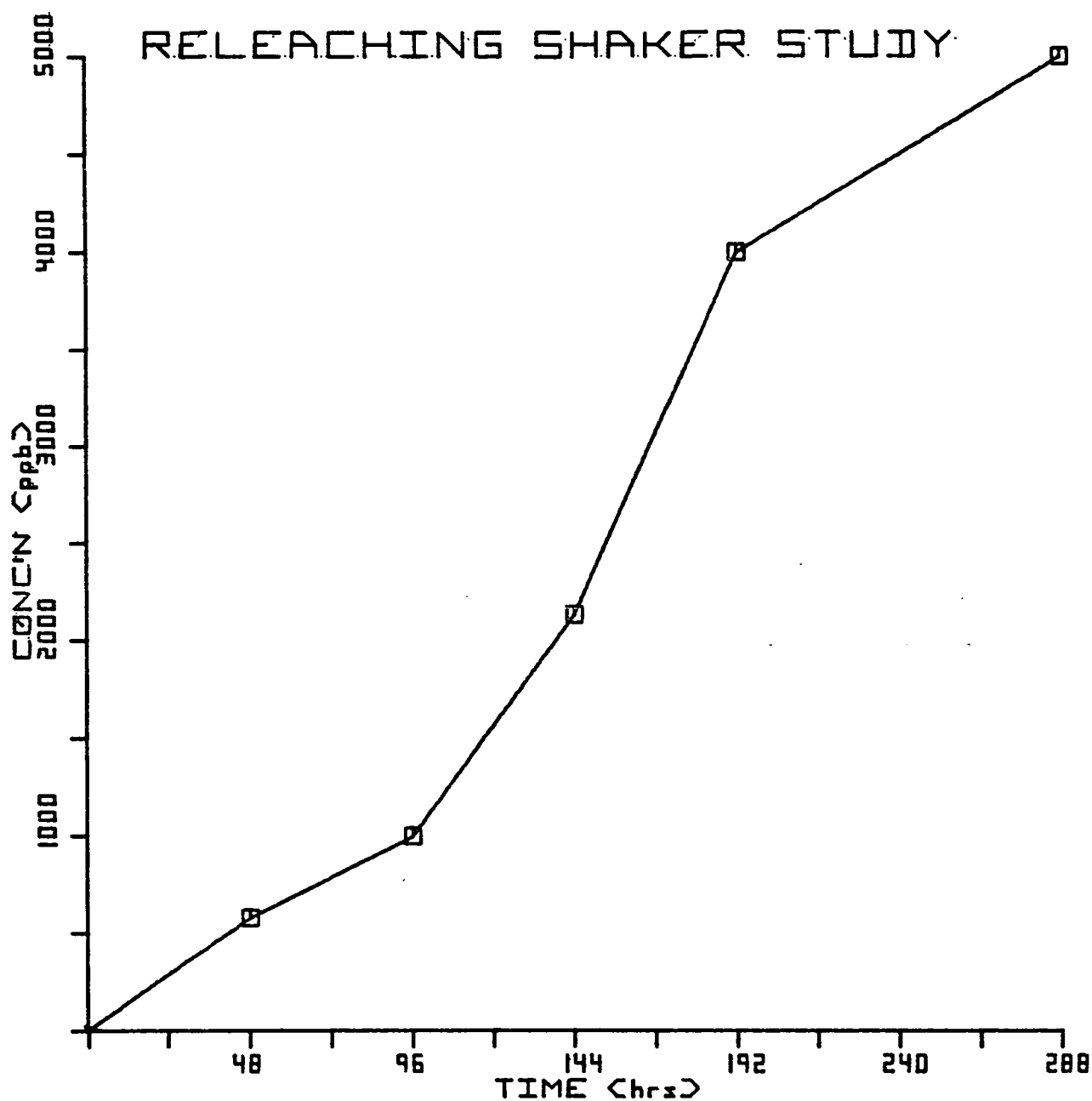COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE

RELEACHING SHAKER STUDY

FIGURE V-D-25:  BARIUM
WESTERN COAL NO. 1 <0.25-0.50 MM>
ACETATE BUFFER LEACHANT
COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE

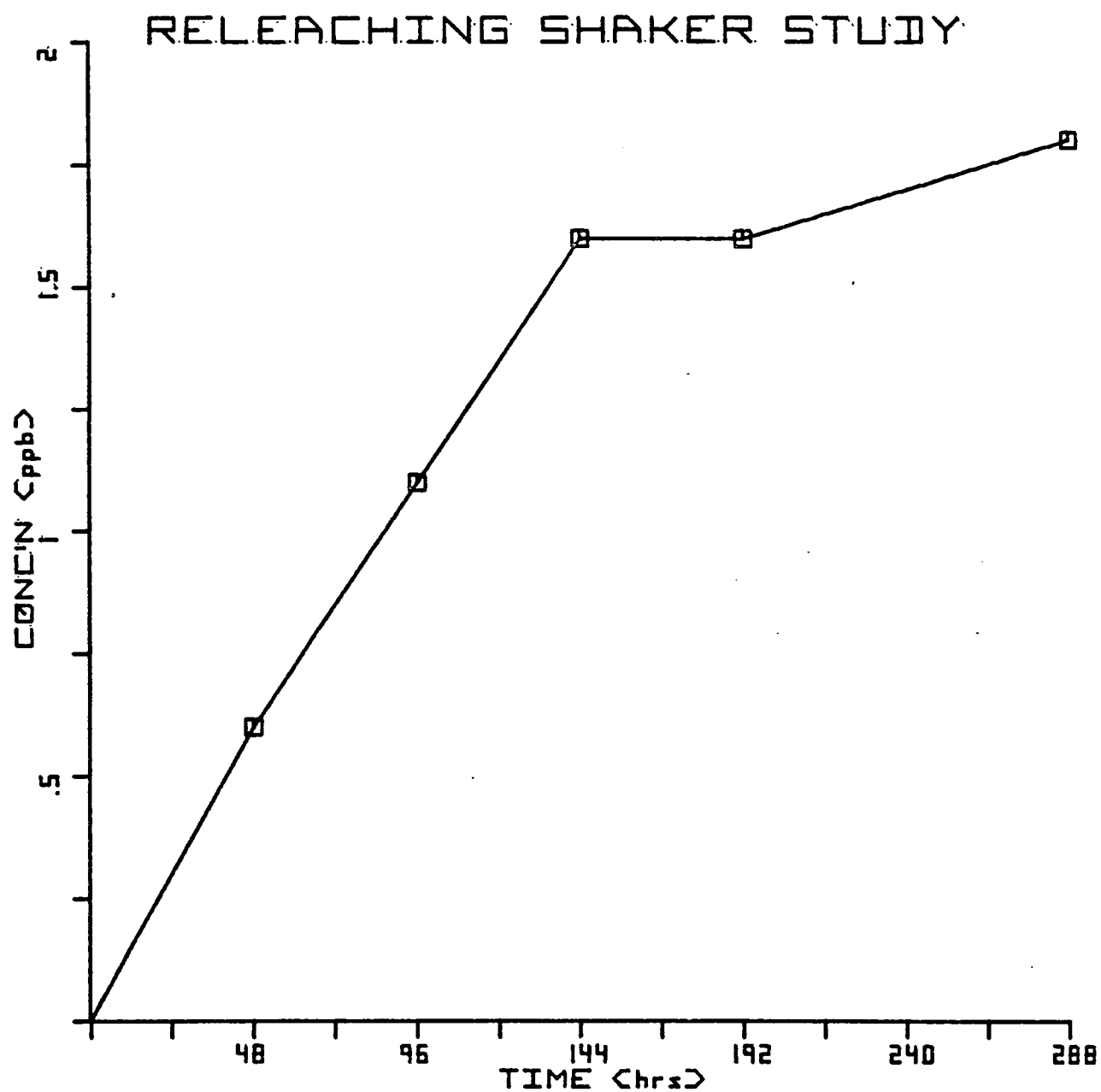FIGURE V-D-26:    CADMIUM
WESTERN COAL NO. 1 <0.25-0.50 MM>
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO = 0.2 G./1.0 G
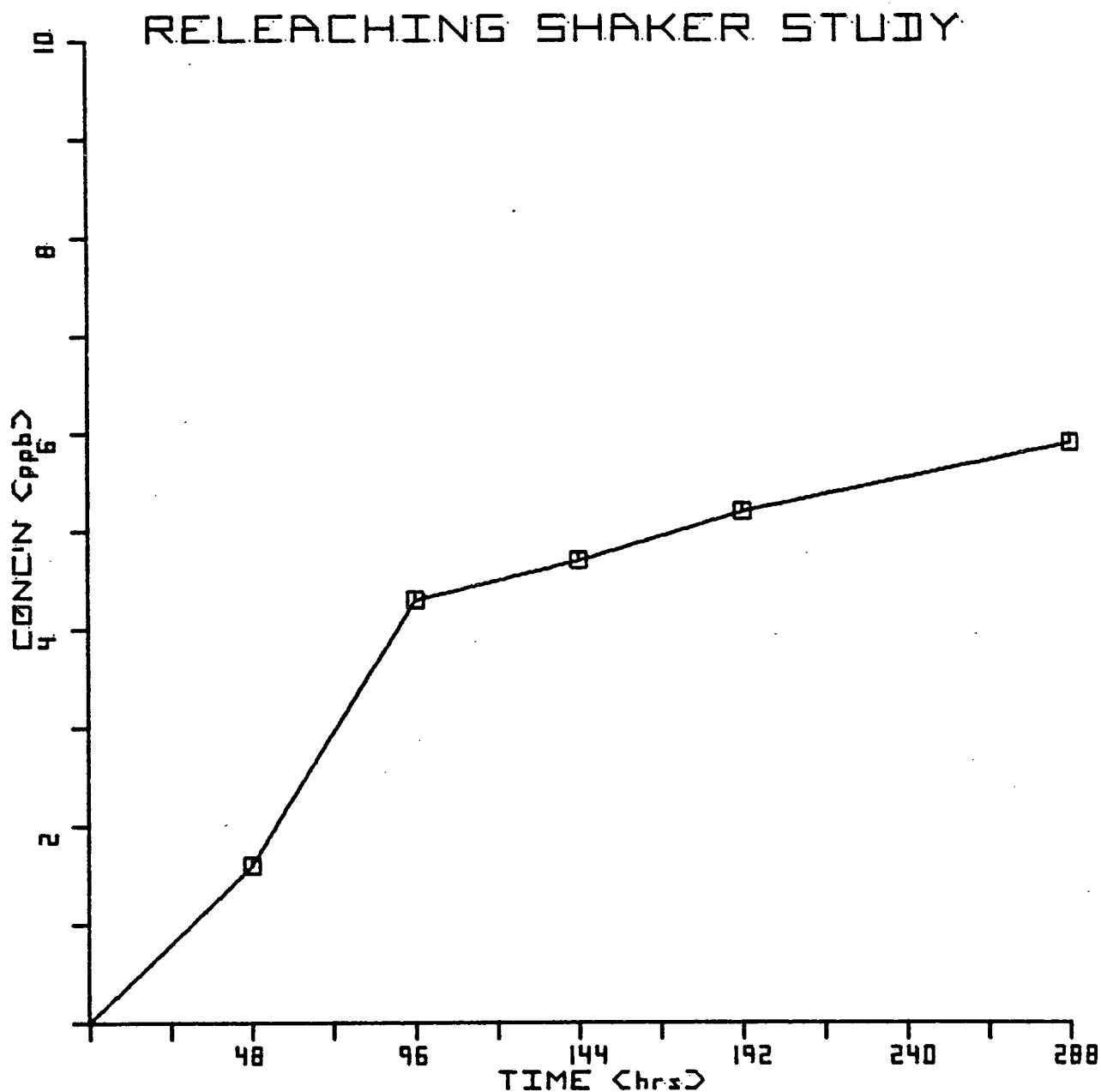AIR ATMOSPHERE
TOTAL RELEASE

# RELEACHING SHAKER STUDY



FIGURE V-D-27: CADMIUM
WESTERN COAL NO. 1 (0.25-0.50 MM)
ACETATE BUFFER LEACHANT
COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
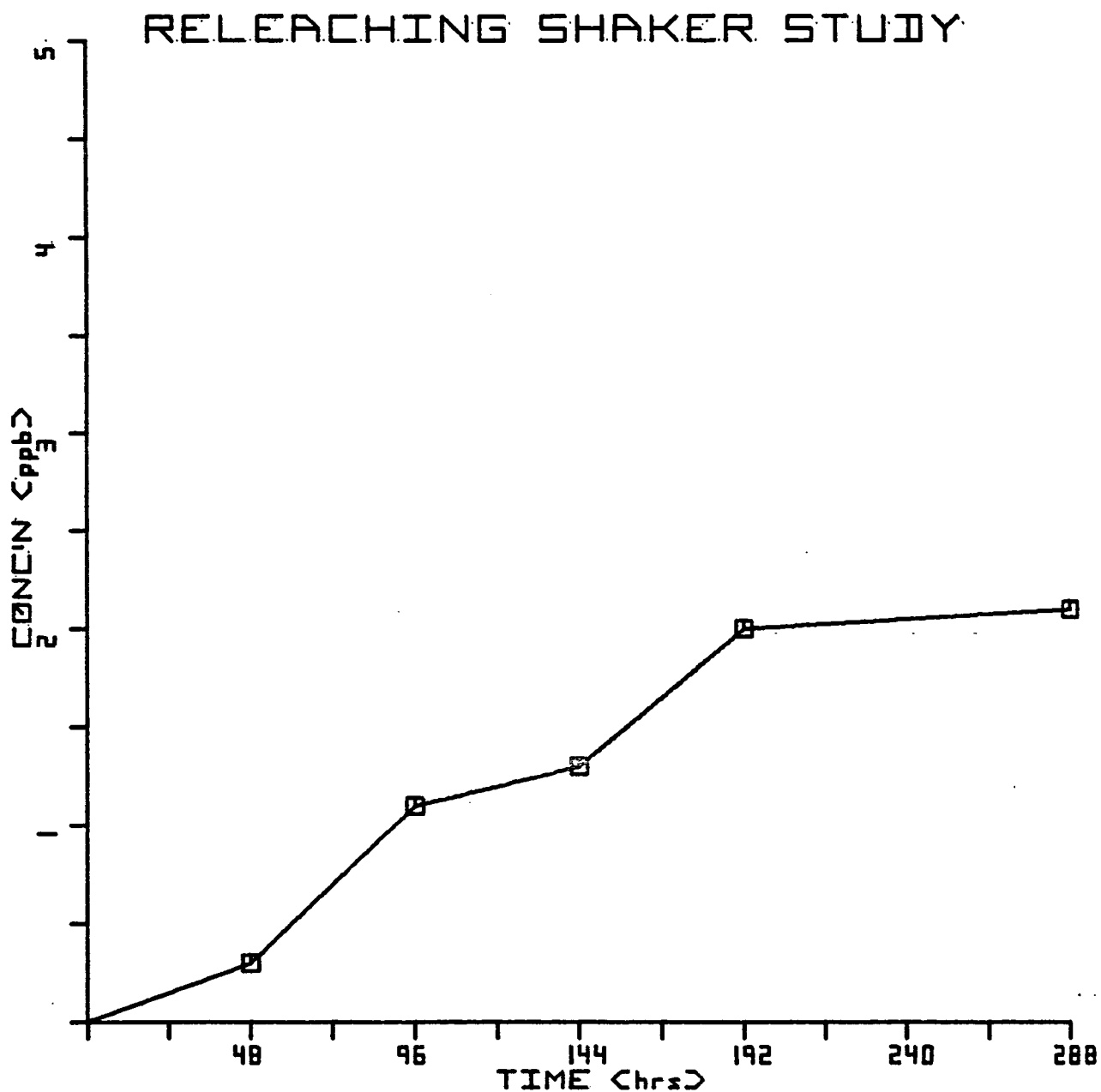TOTAL RELEASE

# RELEACHING SHAKER STUDY



FIGURE V-D-28:    CHROMIUM
WESTERN COAL NO. 1 (0.25-0.50 MM)
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE

FIGURE V-D-29: CHROMIUM
WESTERN COAL NO. 1 <0.25-0.50 MM>
ACETATE BUFFER LEACHANT
COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE

# RELEACHING SHAKER STUDY



FIGURE V-D-30: COBALT
WESTERN COAL NO. 1 <0.25-0.50 MM>
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE

FIGURE V-D-31: COBALT
WESTERN COAL NO. 1 <0.25-0.50 MM>
ACETATE BUFFER LEACHANT
COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE

RELEACHING SHAKER STUDY

FIGURE V-D-32:    COPPER
WESTERN COAL NO. 1 <0.25-0.50 MM>
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE
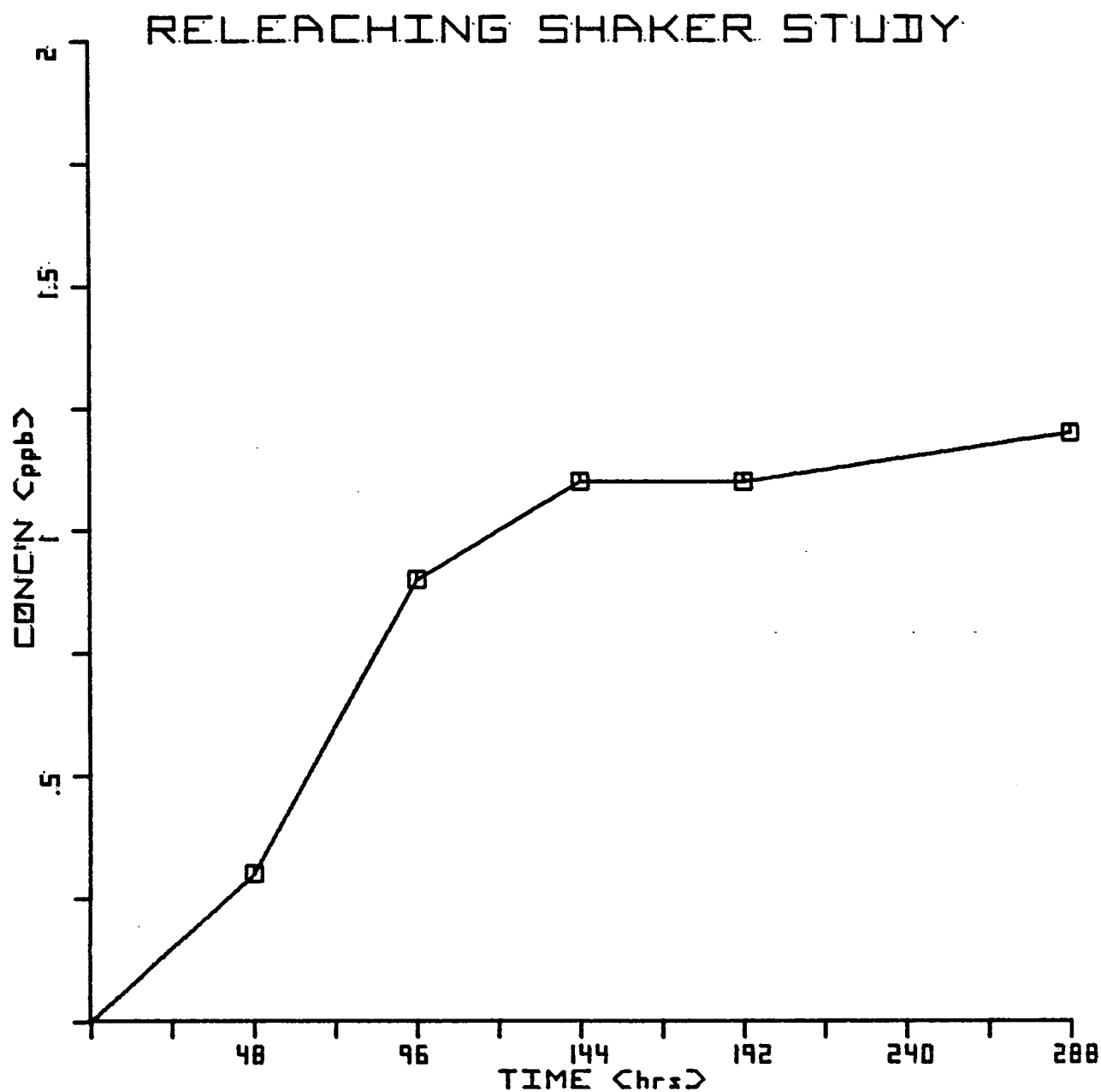
FIGURE V-D-33:    COPPER
                  WESTERN COAL NO. 1 <0.25-0.50 MM>
                  ACETATE BUFFER LEACHANT
                  COAL/LEACHANT RATIO : 0.2 G./1.0 G
                  AIR ATMOSPHERE
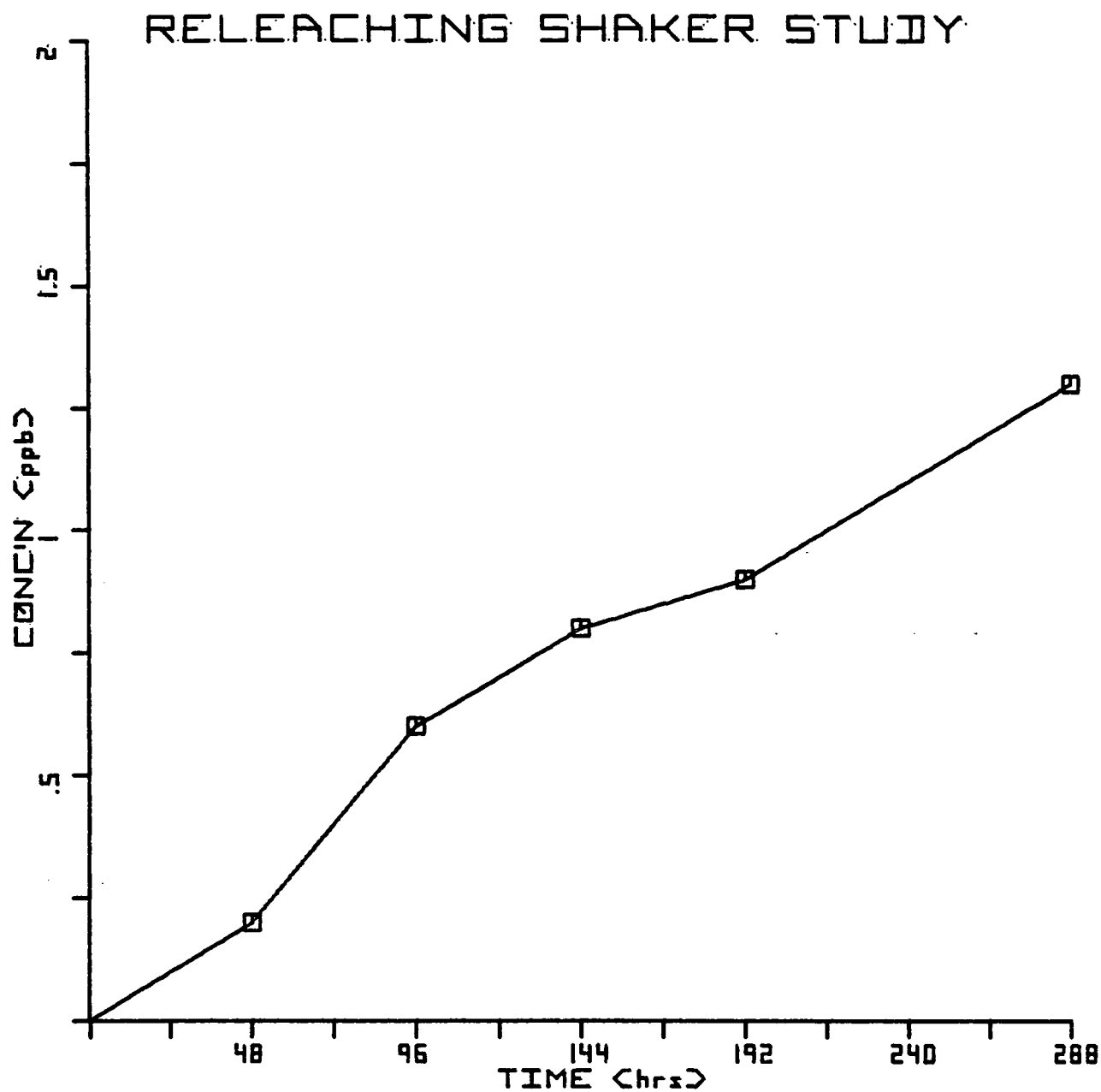                  TOTAL RELEASE

FIGURE V-D-34:    MANGANESE
WESTERN COAL NO. 1 (0.25-0.50 MM)
DEIONIZED WATER LEACHANT
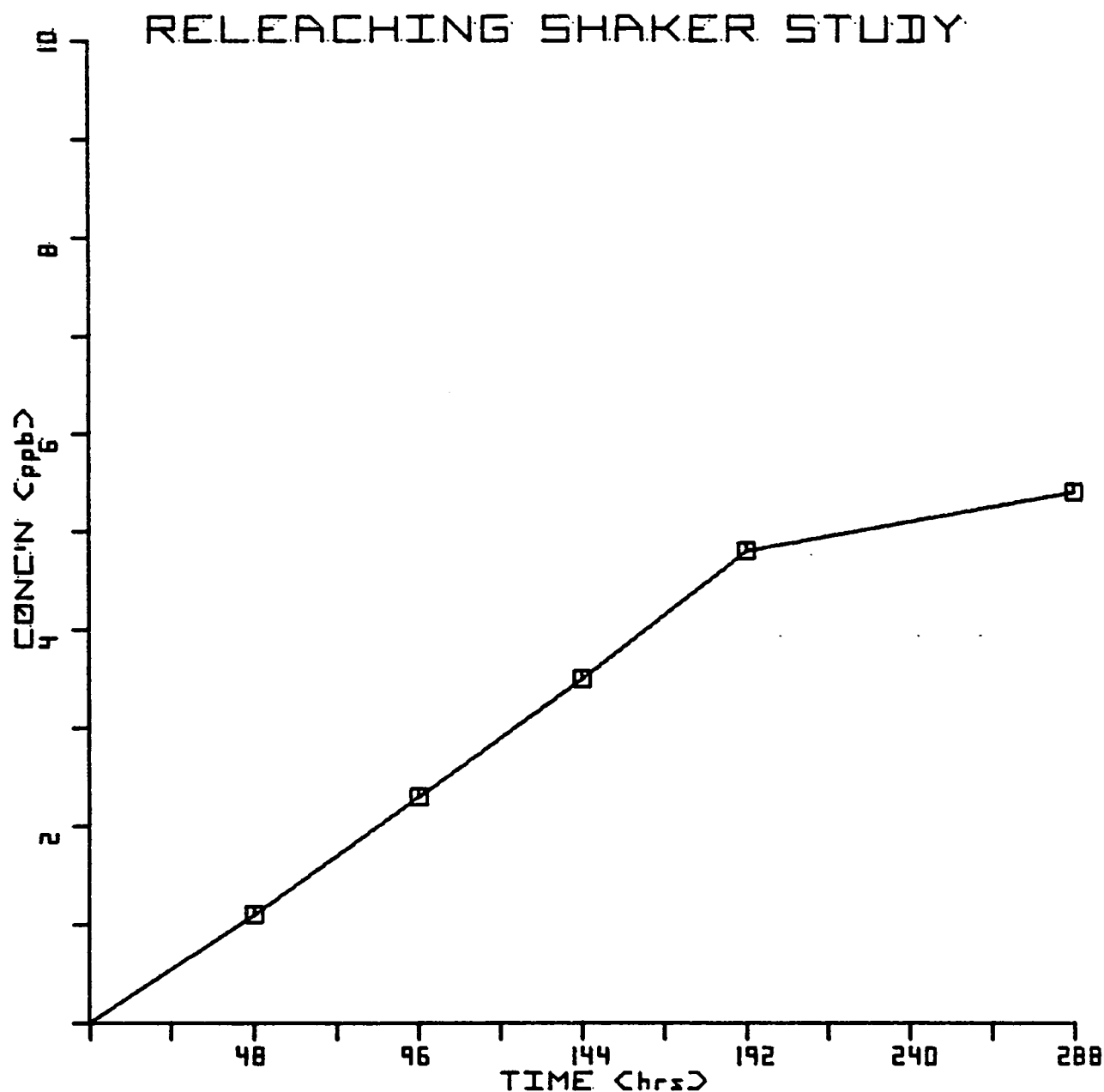COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE

FIGURE V-D-35: MANGANESE
WESTERN COAL NO. 1 (0.25-0.50 MM)
ACETATE BUFFER LEACHANT
COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE

RELEACHING SHAKER STUDY

FIGURE V-D-36:    MOLYBDENUM
WESTERN COAL NO. 1 (0.25-0.50 MM)
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE

# RELEACHING SHAKER STUDY



Figure V-D-37:    MOLYBDENUM
WESTERN COAL NO. 1 (0.25-0.50 mm)
ACETATE BUFFER LEACHANT
COAL/LEACHANT RATIO = 0.2g./1.0g.
AIR ATMOSPHERE
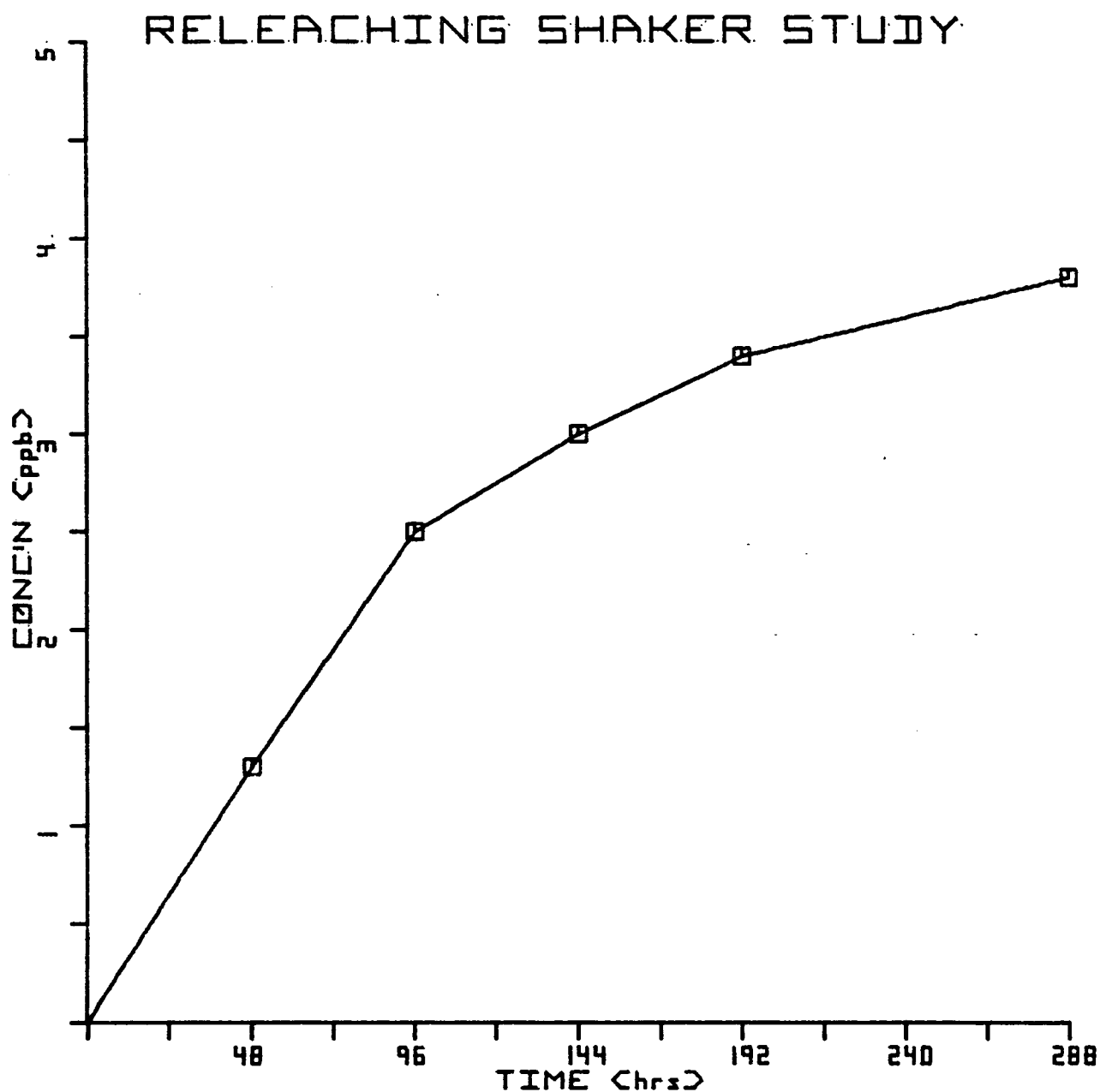TOTAL RELEASE

# RELEACHING SHAKER STUDY



FIGURE V-D-38: SELENIUM
WESTERN COAL NO. 1 (0.25-0.50 MM)
DEIONIZED WATER LEACHANT
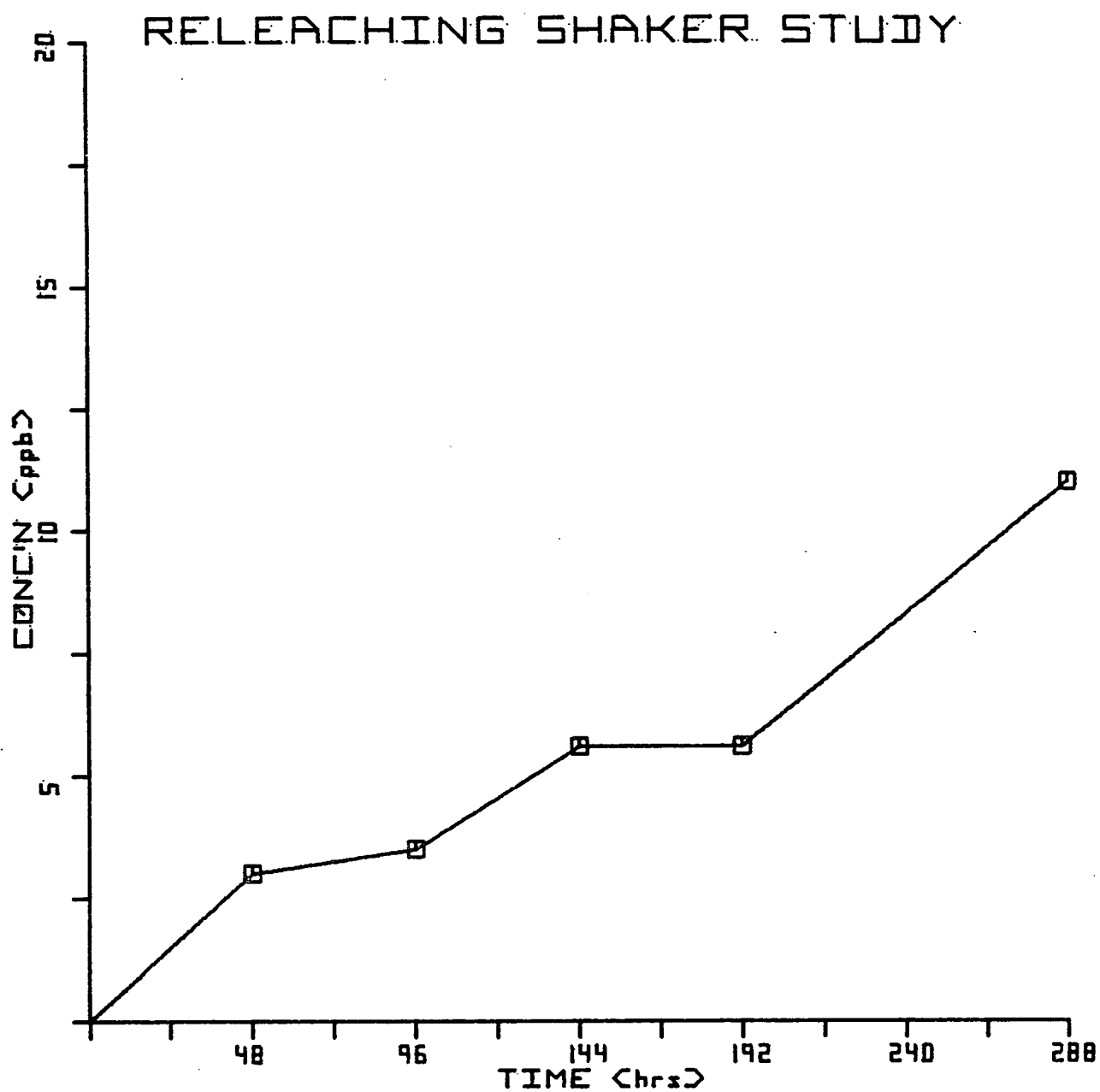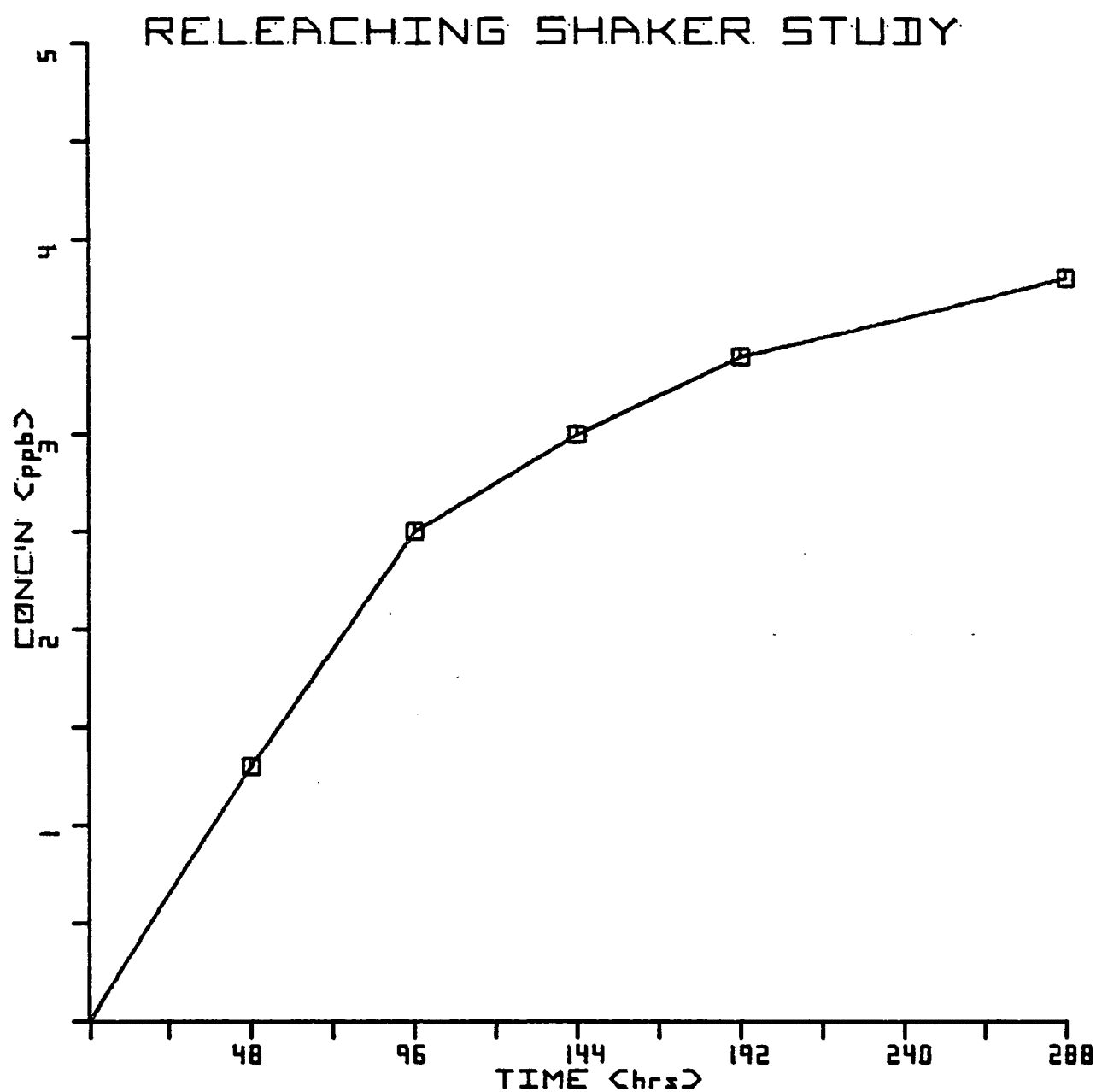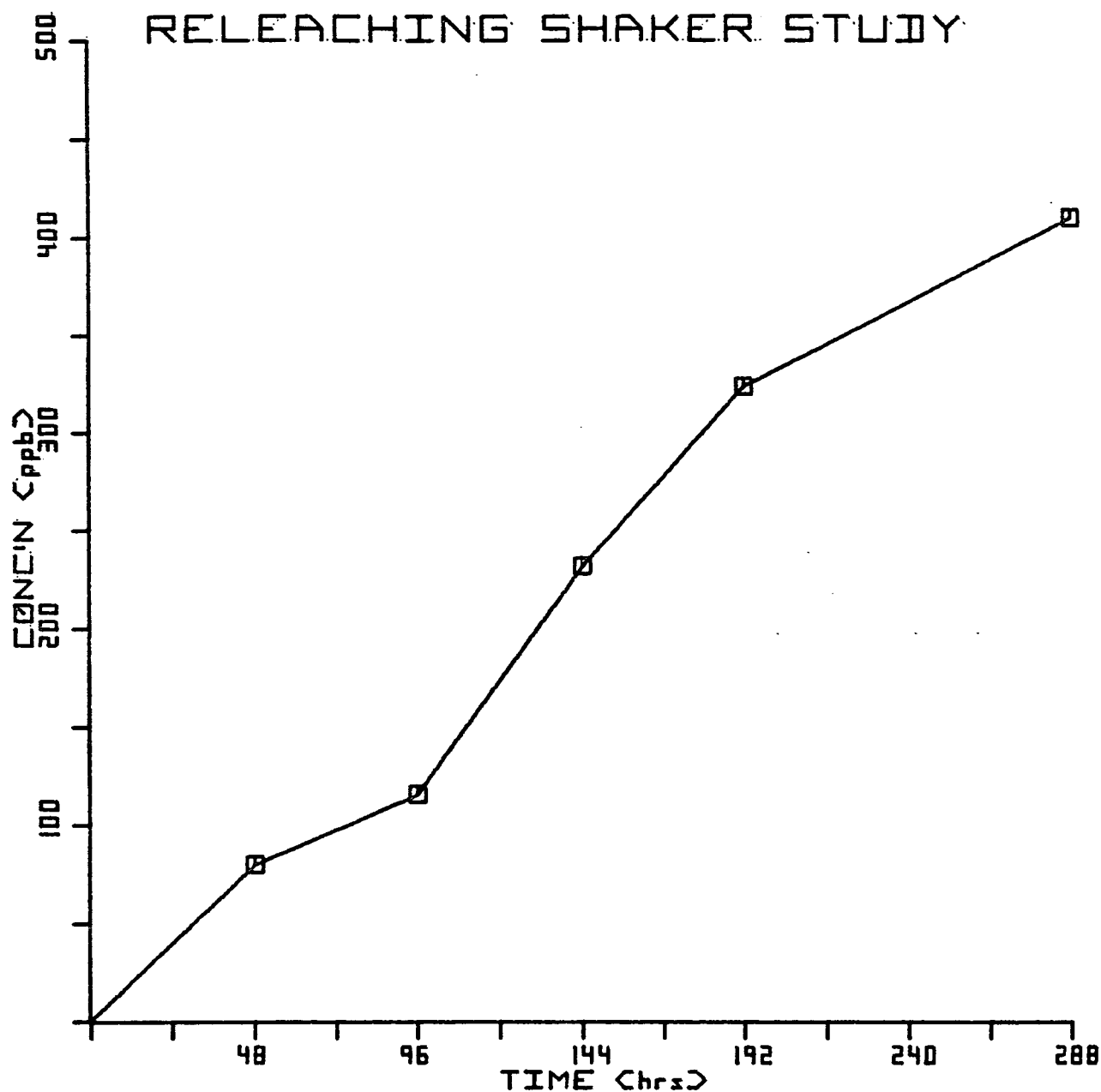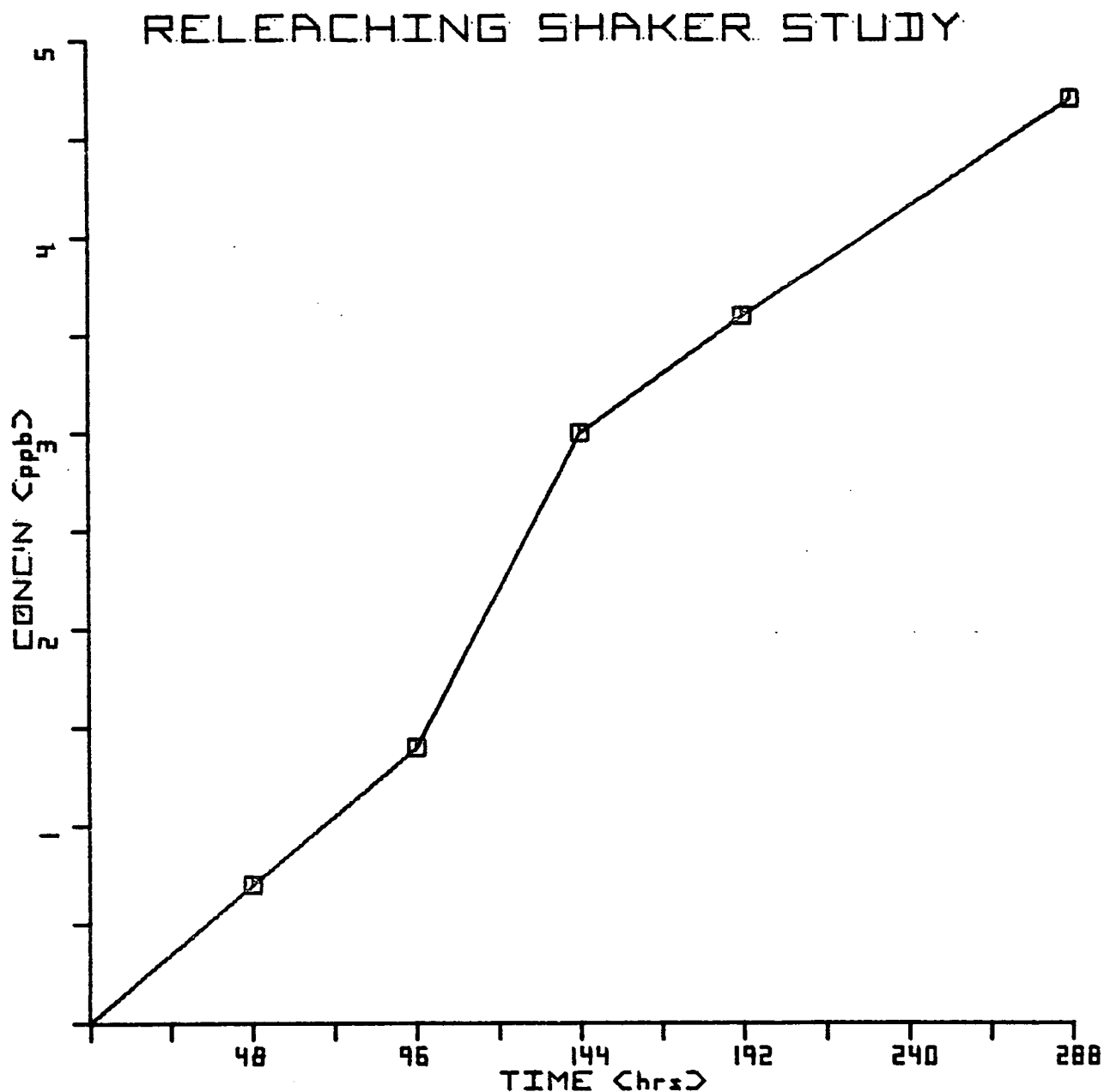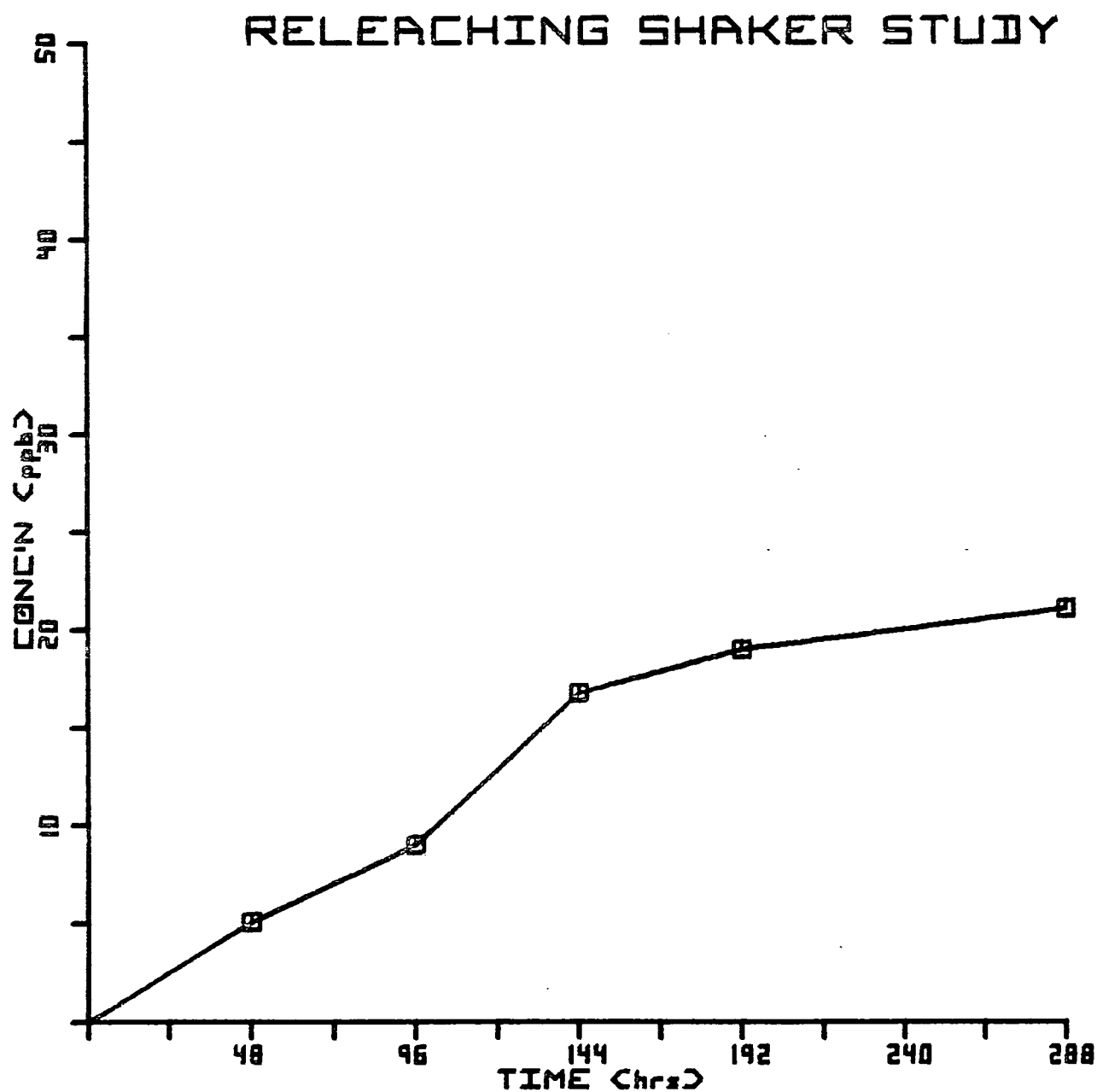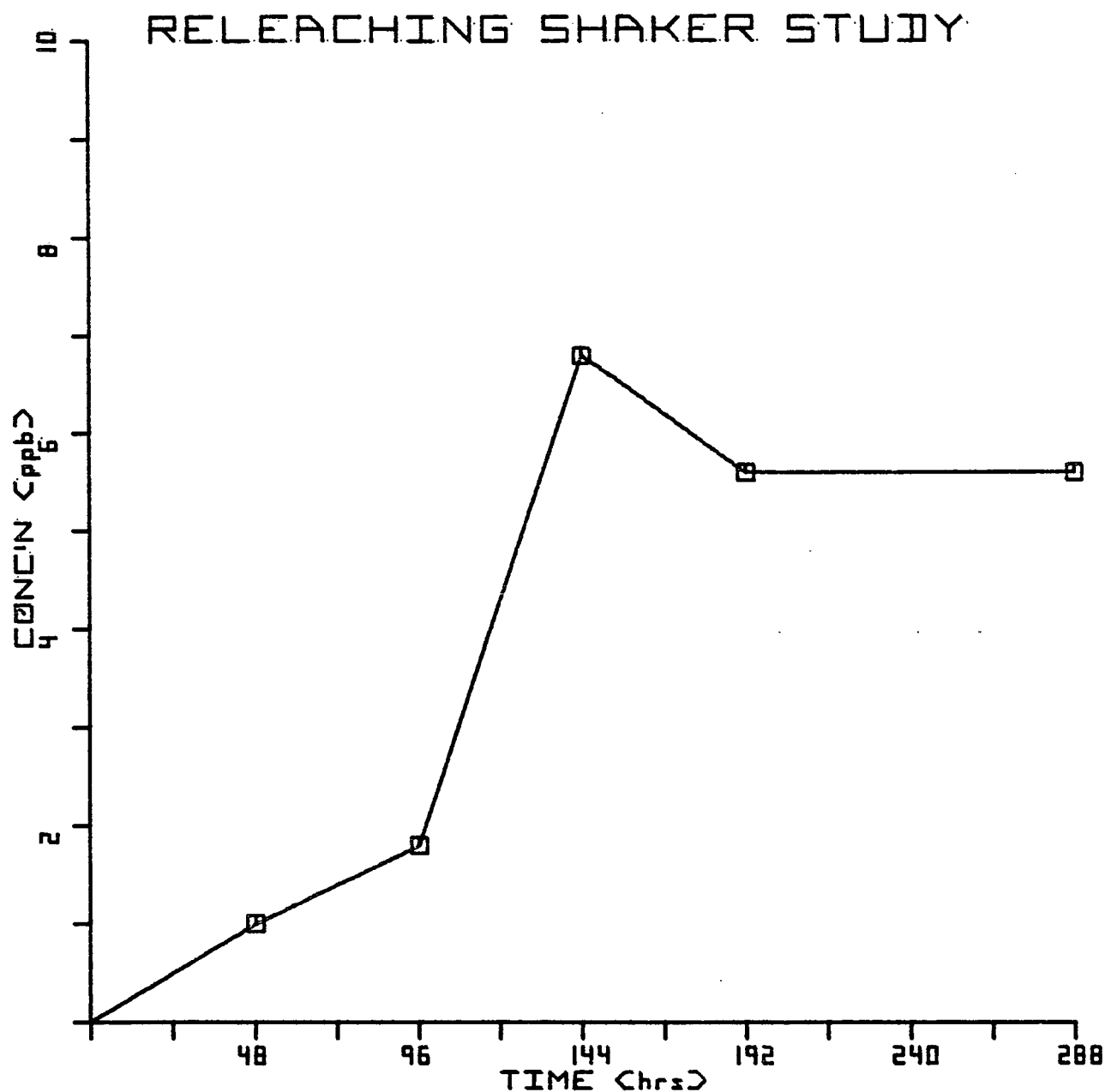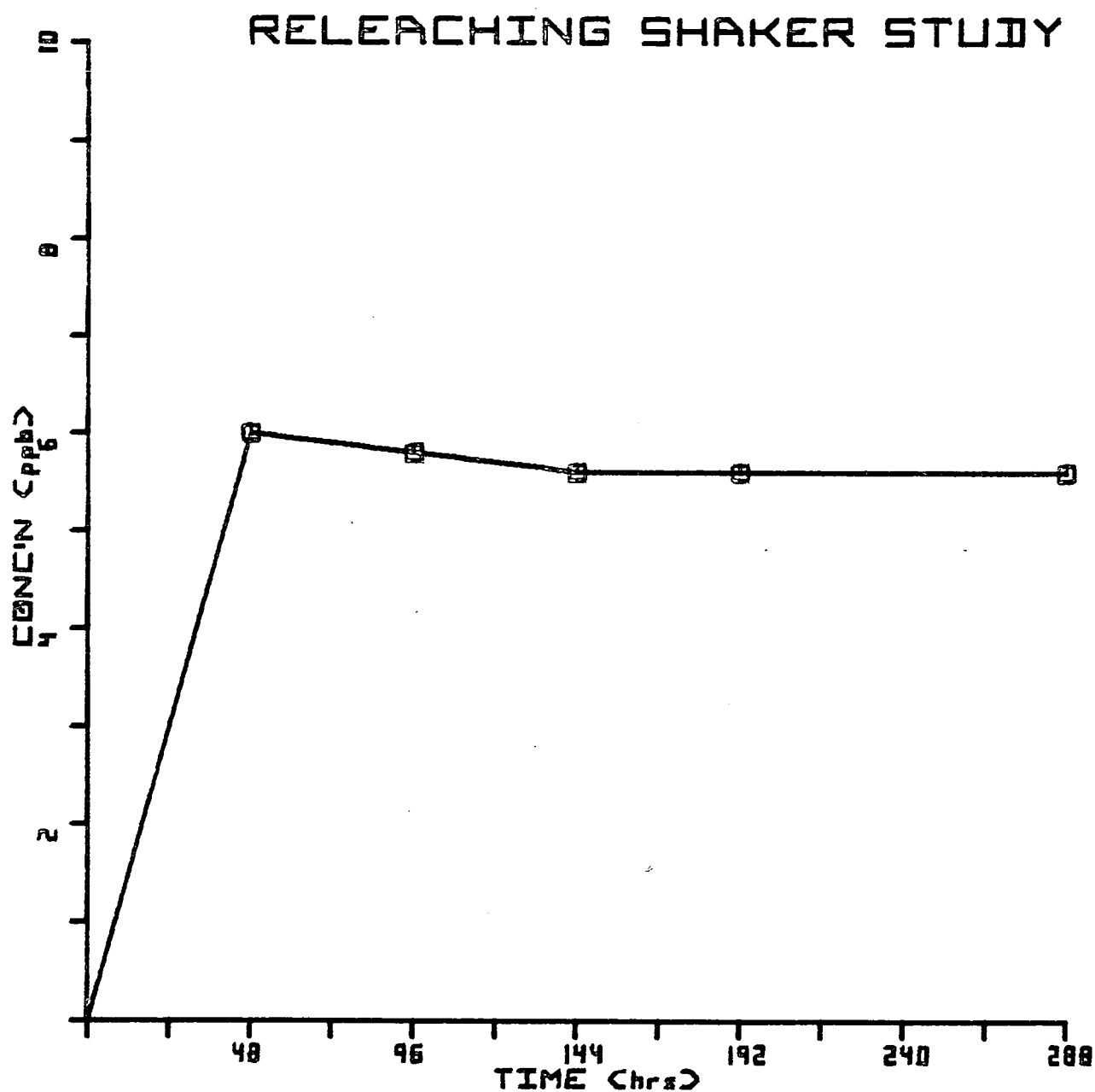COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE

# RELEACHING SHAKER STUDY



FIGURE V-D-39:   SELENIUM
WESTERN COAL NO. 1 (0.25-0.50 mm)
ACETATE BUFFER LEACHANT
COAL/LEACHANT RATIO = 0.2g./1.0g.
AIR ATMOSPHERE
TOTAL RELEASE

## 4. Releaching Factorial Study

a. Experimental--

A five-factor multivariate analysis on metal ion mobility in coal samples was performed. Levels of the variables and the types of controlled variables were as listed in Table V-D-15.

TABLE V-D-15. VARIABLES FOR RELEACHING FACTORIAL STUDY

| Variable | Symbol | Level 1 | Level 2 | Level 3 |
|----------|--------|---------|---------|---------|
| Coal | C | Western #2 | Eastern | --- |
| Water Leachant | W | Deionized | Lake Water | --- |
| Gas (atmosphere) | G | $N_2$ | $O_2$ | --- |
| Time (hours) | H | 24 hr | 48 hr | --- |
| Number of Leaches | L | 1st Leach | 2nd Leach | 3rd Leach |

The previous factorial analysis had determined the general effects of temperature, rate of circulation of leachant and particle size of the coal samples. These variables have significant effects, but not of extremely large magnitude. Therefore, these variables were eliminated from this study. Temperature was maintained at 37°C, while leachant was circulated through the 0.500-1.00 mm coal at a constant flow rate of 40 ml/min. Self-buffering actions of the coals were allowed to control the pH of the systems. This was done to approximate the behavior to be expected under industrial handling and storage.

b. Discussion of Variables--

Coal -     The coal samples that were used were of two types: (1) A sample of western coal (hereafter referred to as Western Coal No. 2) was obtained from the main coal pile at the ORBA transshipment facility by digging down to a depth of approximately two meters (five to six feet) and removing a representative sample of material. It was assumed that this sample was unchanged by the local Duluth-Superior environment. (2) A sample of eastern coal (hereafter referred to as Eastern Coal) was obtained through Detroit-Edison Company.

The rationale for the use of these two types of coal was two-fold. First, would be to determine if there were large differences in the behavior of the two coals. Secondly, the use of the Eastern Coal would partially demonstrate the feasibility and applicability of the current system to other types of coal.

113

Particle size of coal used in the releaching factorial study was in the 0.500-1.00 mm size range.

Water -        Two types of water were chosen for this experiment. Deionized water and unfiltered Lake Superior water which was obtained from the lake water inlet at the Environmental Research Laboratory (ERL) at Duluth, Minnesota. Rationale for the choice of these leachants was to determine the presence (or absence) of materials in the natural waters which would affect the mobilization of metals in the coals.

Gas -          Two atmospheres were maintained over the recirculating leachant. One was purified oxygen, the other purified nitrogen.

Time -         Previous studies show fairly extensive fluctuations in mobilized metal ion concentrations during the early portions of a run. It was felt that the use of an initial sampling time of 24 hours would allow stabilization of the system, and the 48 hour period marked the changeover between successive charges of fresh leachant.

Leaches -      Each of the leaches were allowed to remain in contact with the coal sample for 24 hours. At that point, 100 ml (10% of the leachate volume) of liquid was withdrawn for analyses and replaced immediately with an equal volume of fresh leachant. At the end of 48 hours contact time, 800 ml of leachate was removed and an equivalent volume of fresh leachant was added. A total of three changes of leachant were used.

Procedure -    A charge of 200 grams of 0.500-1.00 mm sized coal and 1000 ml of leachate was placed in the continuous flow system. The leachant was allowed to circulate for a period of 24 hours, at which time a 100 ml sample was withdrawn and an equal volume replaced as previously described. At 48 and 96 hours, 800 ml of leachate were removed and replaced with fresh charges of leachant. Samples were taken at 72 and 120 hours using the same procedure as for the 24 hour samples.

The samples which were removed from the system were split into two portions. One portion was used to determine the current pH level of the circulating fluid. The other portion was filtered with suction through a 0.45 micron membrane filter and the filtered sample was stabilized with nitric acid. A separate portion of the filtered sample was treated with potassium dichromate to stabilize it for later mercury analysis. As controls: Blanks and 'spiked' blanks were also run under the same experimental conditions.

Analyses were performed for all metals involved in the study, including mercury, by flameless atomic absorption spectrophotometry.[1, 2, 10, 11, 15, 16]

114

c.  Results and Discussion--

The data from the lake water leached runs is not considered reliable enough to report. The experimental plan was to use fresh lake water for each run, thus reducing any effects of laboratory storage. Also, the lake water was not filtered because particulate matter was considered a natural part of the medium. Unfortunately, the different samples of lake water showed very wide variations in metal content which precluded any reasonable analysis of the data.

The results of the deionized water runs are given in Tables V-D-16 and V-D-17. The data were analyzed on a PDP 11/70 computer using "ANOVAR" (a library supplied analysis of variance program). Detailed results, by metal, are as follows:

Arsenic -  Western Coal No. 2:  There were no significant variables. The raw data were below detection limits.

Eastern Coal:  Significant variables were:

L       $\alpha < 0.005$
G       $\alpha < 0.01$
HL      $\alpha < 0.05$

The L and G dependences are shown in Fig. V-D-40.

Barium -  Western Coal No. 2:  There were no significant variables. The raw data were below detection limits.

Eastern Coal:  Significant variables were:

G       $\alpha < 0.01$
L       $\alpha < 0.10$

The L and G dependences are shown in Fig. V-D-41.

Cadmium -  Western Coal No. 2:  There were no significant variables.

Grand Mean = 0.33 ppb;  s = 0.15 ppb

Eastern Coal:  There were no significant variables.

Grand Mean = 3.94 ppb;  s = 0.64 ppb

Chromium -  Western Coal No. 2:  There were no significant variables. The raw data were below detection limits.

Eastern Coal:  Significant variables were:

G       $\alpha < 0.0025$
LG      $\alpha < 0.10$

The L and G dependences are shown in Fig. V-D-42.

Cobalt -  Western Coal No. 2:  There were no significant variables. The raw data were below detection limits.

Eastern Coal:  Significant variables were:

G       $\alpha < 0.01$

115

L       $\alpha < 0.05$
LG      $\alpha < 0.10$

The L and G dependences are shown in Fig. V-D-43.

Copper -    Western Coal No. 2:  Significant variables were:

L       $\alpha < 0.001$
G       $\alpha < 0.025$

The L and G dependences are shown in Fig. V-D-44.

Eastern Coal:  Significant variables were:

L       $\alpha < 0.001$
G       $\alpha < 0.001$
LG      $\alpha < 0.001$
HG      $\alpha < 0.005$
H       $\alpha < 0.01$

The L and G dependences are shown in Fig. V-D-45.

Lead -      Western Coal No. 2:  G was significant with $\alpha < 0.10$ but all but one raw data point out of twelve were below single point detection limits so no plot was made.

Eastern Coal:  The statistics were confused and only two out of twelve raw data points were above detection limits so no plot was made.

Manganese - Western Coal No. 2:  The only significant variable was G at $\alpha < 0.10$.  The mean, total releases from $N_2$ and $O_2$ are:

0.74 ppb for $N_2$
2.40 ppb for $O_2$

Eastern Coal:  Significant variables were:

G       $\alpha < 0.001$
L       $\alpha < 0.10$

The L and G dependences are shown in Fig. V-D-46.

Mercury -   Only the $N_2$ run for mercury was analyzed.  With the exception of one sample which seemed to be obviously contaminated, the Hg concentrations were quite low.  No significant trends appeared.

Molybdenum - Western Coal No. 2:  The variables H, L and G showed high significance but the raw data were below single point detection limits.  No plots were made.

Eastern Coal:  All Mo concentrations were zero.

Nickel -    Western Coal No. 2:  Significant variables were:

G       $\alpha < 0.10$
L       $\alpha < 0.10$

116

The L and G dependences are shown in Fig. V-D-47.

Eastern Coal:  Significant variables were:

G        $\alpha < 0.01$
L        $\alpha < 0.10$

The L and G dependences are shown in Fig. V-D-48.

Selenium -    Western Coal No. 2:  There were no significant variables and the mean was below detection limits.  No plot was made.

Eastern Coal:  The only significant variable was L with $\alpha < 0.01$.  There was a reasonable but not significant G effect.  The raw data were very near single point detection limits.

Even though the data are doubtful, the L and G dependences are shown in Fig. V-D-49.

Vanadium -    Western Coal No. 2:  Significant variables were:

G        $\alpha < 0.001$
L        $\alpha < 0.025$
LG       $\alpha < 0.025$

The data for $N_2$ were all zero.  The L dependence is shown in Fig. V-D-50.

Eastern Coal:  All V concentrations were zero.

Zinc -        Western Coal No. 2:  Significant variables were:

G        $\alpha < 0.001$
L        $\alpha < 0.01$
LG       $\alpha < 0.05$

The L and G dependences are shown in Fig. V-D-51.

Eastern Coal:  There were no significant variables.  The total release grand mean for Zn was 154 ppb.

General Discussion of Results--
    The most obvious result of these runs is the fact that Western Coal No. 2 showed very different leaching behavior than Western Coal No. 1.  Specifically, comparing these results with the results for the continuous flow releaching runs (done on Western Coal No. 1) one sees that there was much more leachable metal in Western Coal No. 1.  No control of or knowledge of the actual mine sites were available for this work.  The most probable assumption is that the Western Coal No. 2 sample was taken from an aquifer vein and was thus already thoroughly leached.  The EDTA runs also clearly show this comparison between the two samples of western coal.

    For the few metals which show significant leaching from the western coal, both gas saturation and number of releachings show significant effects.  All metals except zinc show increased leaching with oxygen saturation.

117

The Western Coal No. 2 also seems to show somewhat higher pH values in the leachate than Western Coal No. 1. This could, of course, be caused by alkaline water in the aquifer.

The Eastern Coal shows higher concentrations in the leachate for all metals except molybdenum and vanadium. The pH of the leachate from eastern coal is much lower than leachate from the western coals. These effects are as expected.

Oxygen saturation increases leaching in the Eastern Coal in all cases except barium.

Overall, the following trends emerge:

1.  Eastern Coal is acidic and leaches more metals than western coal.

2.  There are pronounced differences between different samples of western coal.

3.  Oxygen enhances leaching in most cases.

TABLE V-D-16

Releaching Factorial Western #2 Coal Deionized Water Leaching

| Levels | | | | Total Release Concentrations in ppb | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | L | G | pH | As | Ba | Cd | Cr | Co | Cu | Pb | Mn | Hg | Mo | Ni | Se | V | Zn |
| 1 | 1 | 1 | 7.62 | 0.50 | 5.0 | 0.70 | 0.10 | 0.0 | 2.40 | 0.0 | 2.60 | 0.06 | 0.00 | 2.0 | 0.0 | 0.0 | 2.0 |
| 2 | 1 | 1 | 7.48 | 0.05 | 2.5 | 0.27 | 0.21 | 0.0 | 1.54 | 0.0 | 0.36 | 0.15 | 0.60 | 0.2 | 0.0 | 0.0 | 6.2 |
| 1 | 2 | 1 | 7.91 | 0.05 | 2.1 | 0.33 | 0.17 | 0.0 | 3.28 | 0.0 | 0.44 | 3.98* | 0.48 | 1.2 | 0.0 | 0.0 | 10.0 |
| 2 | 2 | 1 | 7.62 | 0.05 | 2.1 | 0.34 | 0.17 | 0.0 | 3.88 | 0.0 | 0.35 | 0.51 | 1.08 | 1.3 | 0.0 | 0.0 | 13.5 |
| 1 | 3 | 1 | 8.02 | 0.05 | 2.1 | 0.42 | 0.17 | 0.1 | 5.40 | 0.0 | 0.35 | 0.51 | 0.96 | 1.1 | 0.0 | 0.0 | 12.9 |
| 2 | 3 | 1 | 8.30 | 0.05 | 2.1 | 0.33 | 0.17 | 0.2 | 5.01 | 0.0 | 0.35 | 0.51 | 0.96 | 3.1 | 1.0 | 0.0 | 13.0 |
| 1 | 1 | 2 | 7.64 | 0.50 | 2.0 | 0.10 | 0.10 | 0.0 | 1.50 | 0.0 | 0.10 | -- | 0.50 | 0.0 | 1.0 | 3.0 | 1.0 |
| 2 | 1 | 2 | 7.59 | 0.05 | 4.2 | 0.11 | 0.11 | 0.0 | 2.85 | 0.0 | 1.91 | -- | 0.95 | 2.0 | 0.1 | 16.3 | 1.1 |
| 1 | 2 | 2 | 7.80 | 0.05 | 3.4 | 0.29 | 0.09 | 0.0 | 3.91 | 0.10 | 5.33 | -- | 1.27 | 1.6 | 0.1 | 36.1 | 1.9 |
| 2 | 2 | 2 | 7.78 | 0.55 | 5.4 | 0.31 | 0.19 | 0.0 | 5.47 | 0.41 | 2.31 | -- | 1.32 | 4.6 | 0.1 | 28.5 | 2.0 |
| 1 | 3 | 2 | 7.77 | 0.95 | 7.0 | 0.37 | 0.27 | 0.0 | 6.27 | 0.33 | 2.33 | -- | 1.22 | 4.0 | 0.1 | 27.9 | 3.8 |
| 2 | 3 | 2 | 7.84 | 0.50 | 5.2 | 0.38 | 0.18 | 0.0 | 6.21 | 0.33 | 2.44 | -- | 1.62 | 6.0 | 2.1 | 30.1 | 3.0 |

TABLE V-D-17

Releaching Factorial Eastern Coal Deionized Water Leaching

| Levels | | | | Total Release Concentrations in ppb | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | L | G | pH | As | Ba | Cd | Cr | Co | Cu | Pb | Mn | Hg | Mo | Ni | Se | V | Zn |
| 1 | 1 | 1 | 3.23 | 0.00 | 43.0 | 4.20 | 1.10 | 106 | 9.30 | 0.20 | 700 | 0.38 | 0.0 | 210 | 0.0 | 0.0 | 220 |
| 2 | 1 | 1 | 3.31 | 0.00 | 36.4 | 3.92 | 0.51 | 109 | 6.44 | 0.02 | 732 | 0.35 | 0.0 | 191 | 0.0 | 0.0 | 143 |
| 1 | 2 | 1 | 3.60 | 0.50 | 34.0 | 3.72 | 0.43 | 110 | 8.44 | 0.02 | 727 | 0.32 | 0.0 | 187 | 1.0 | 0.0 | 169 |
| 2 | 2 | 1 | 3.61 | 0.05 | 39.4 | 3.77 | 0.43 | 107 | 9.16 | 0.02 | 756 | 0.29 | 0.0 | 206 | 0.1 | 0.0 | 151 |
| 1 | 3 | 1 | 3.80 | 0.55 | 42.6 | 4.07 | 0.43 | 111 | 12.9 | 0.02 | 788 | 0.33 | 0.0 | 213 | 1.1 | 0.0 | 155 |
| 2 | 3 | 1 | 3.90 | 0.60 | 46.1 | 4.01 | 0.43 | 115 | 13.9 | 0.02 | 810 | 0.42 | 0.0 | 218 | 2.2 | 0.0 | 155 |
| 1 | 1 | 2 | 3.52 | 1.00 | 22.0 | 2.30 | 1.00 | 107 | 14.2 | 0.10 | 830 | -- | 0.0 | 180 | 0.0 | 0.0 | 65 |
| 2 | 1 | 2 | 3.28 | 1.10 | 26.2 | 3.43 | 1.10 | 114 | 24.0 | 0.01 | 1150 | -- | 0.0 | 238 | 0.0 | 0.0 | 137 |
| 1 | 2 | 2 | 3.21 | 1.90 | 35.4 | 4.79 | 1.00 | 123 | 38.6 | 0.11 | 1170 | -- | 0.0 | 254 | 2.0 | 0.0 | 151 |
| 2 | 2 | 2 | 3.18 | 1.50 | 31.9 | 4.19 | 1.71 | 141 | 47.2 | 0.22 | 1180 | -- | 0.0 | 281 | 2.2 | 0.0 | 152 |
| 1 | 3 | 2 | 3.27 | 1.40 | 35.1 | 4.25 | 1.55 | 147 | 50.9 | 0.18 | 1230 | -- | 0.0 | 300 | 1.8 | 0.0 | 162 |
| 2 | 3 | 2 | 3.08 | 1.90 | 37.6 | 4.68 | 1.95 | 150 | 63.9 | 0.18 | 1300 | -- | 0.0 | 323 | 1.8 | 0.0 | 184 |

FIGURE V-D-40: ARSENIC
EASTERN COAL (0.25-0.50 mm)
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO (0.2 g/1.0 g)
TOTAL RELEASE DATA
□ = OXYGEN SATURATION VALUES
X = NITROGEN SATURATION VALUES

121

FIGURE V-D-41: BARIUM
EASTERN COAL (0.25-0.50 mm)
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO (0.2 g/1.0 g)
TOTAL RELEASE DATA
□ = OXYGEN SATURATION VALUES
X = NITROGEN SATURATION VALUES

FIGURE V-D-42: CHROMIUM
EASTERN COAL (0.25-0.50 mm)
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO (0.2 g/1.0 g)
TOTAL RELEASE DATA
□ = OXYGEN SATURATION VALUES
X = NITROGEN SATURATION VALUES

FIGURE V-D-43: COBALT
EASTERN COAL <0.25-0.50 mm>
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO <0.2 g/1.0 g>
TOTAL RELEASE DATA
□ = OXYGEN SATURATION VALUES
⊠ = NITROGEN SATURATION VALUES
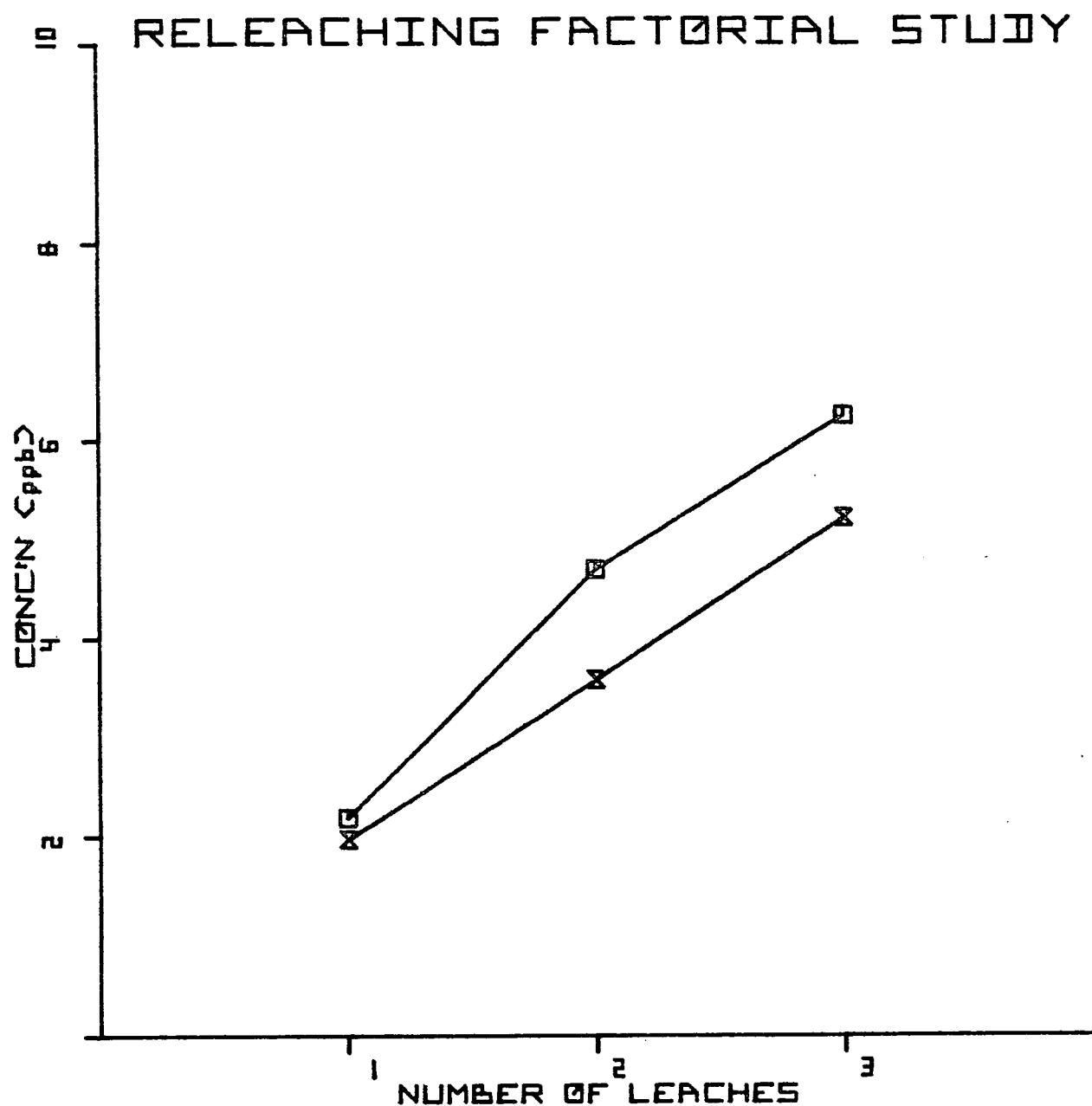
FIGURE V-D-44: COPPER
WESTERN COAL NO. 2 <0.25-0.50 mm>
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO <0.2 g/1.0 g>
TOTAL RELEASE DATA
□ = OXYGEN SATURATION VALUES
X = NITROGEN SATURATION VALUES
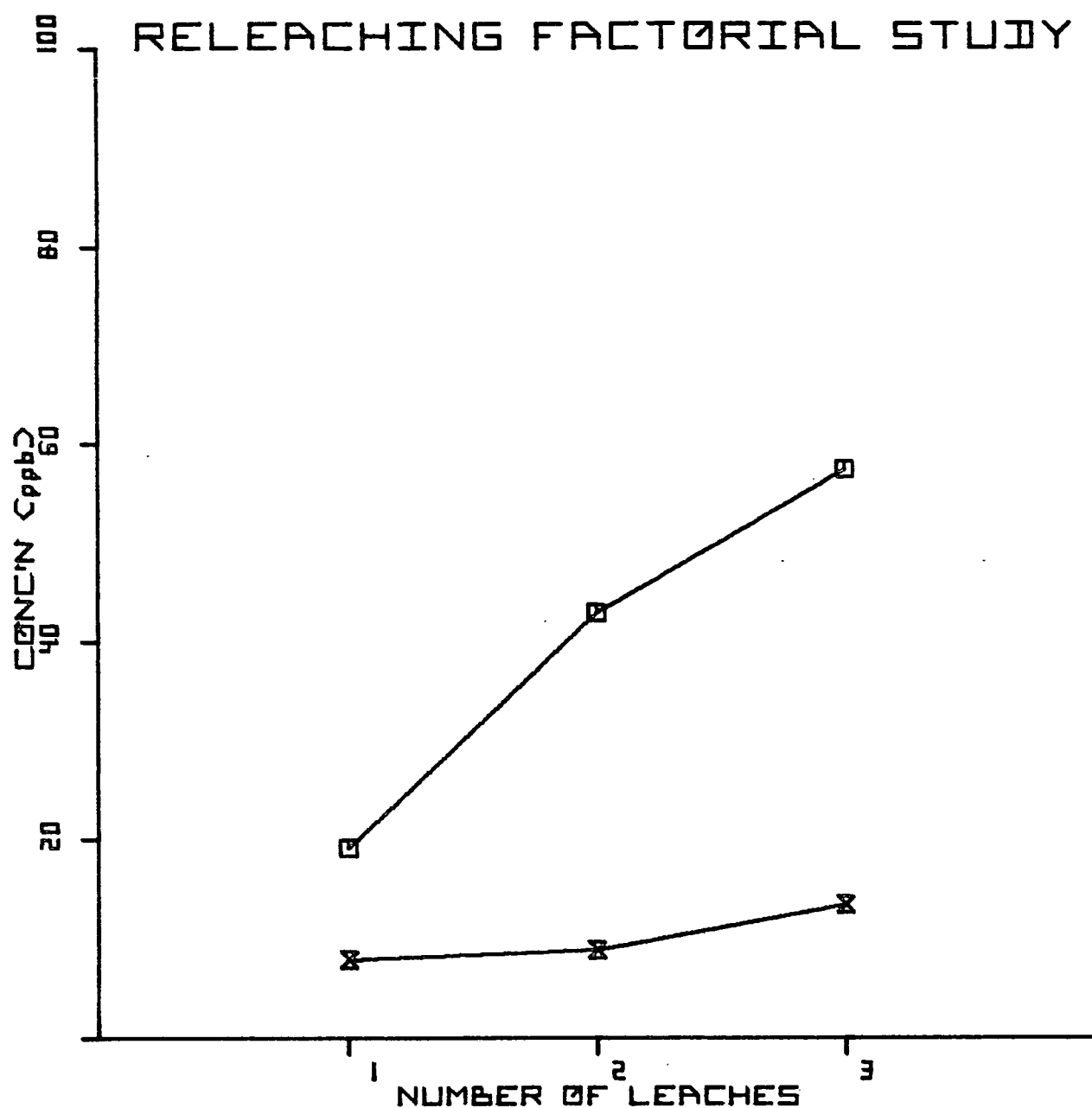
FIGURE V-D-45: COPPER
EASTERN COAL (0.25-0.50 mm)
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO (0.2 g/1.0 g)
TOTAL RELEASE DATA
□ = OXYGEN SATURATION VALUES
X = NITROGEN SATURATION VALUES
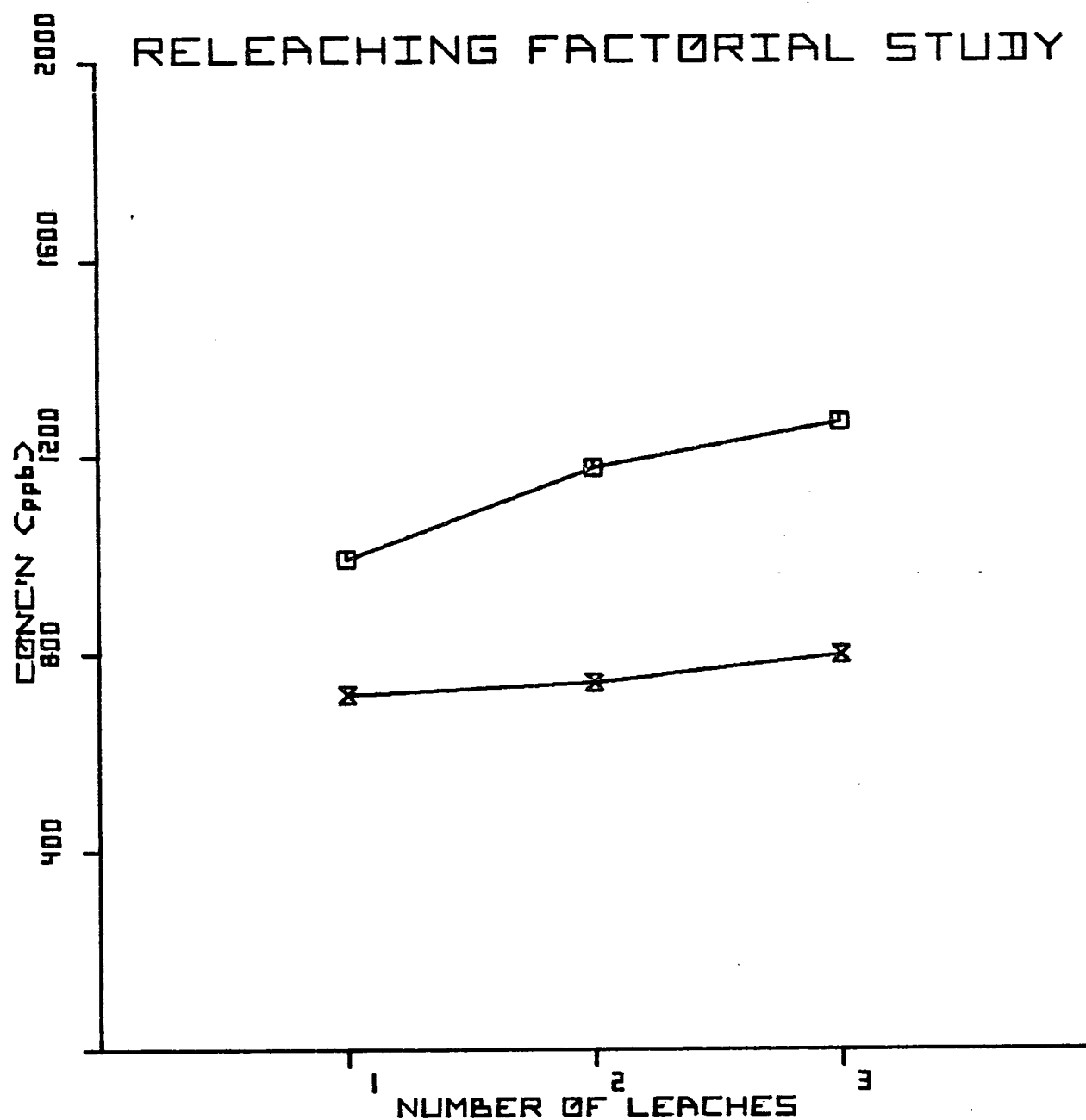
FIGURE V-D-46: MANGANESE
EASTERN COAL (0.25-0.50 mm)
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO (0.2 g/1.0 g)
TOTAL RELEASE DATA
□ = OXYGEN SATURATION VALUES
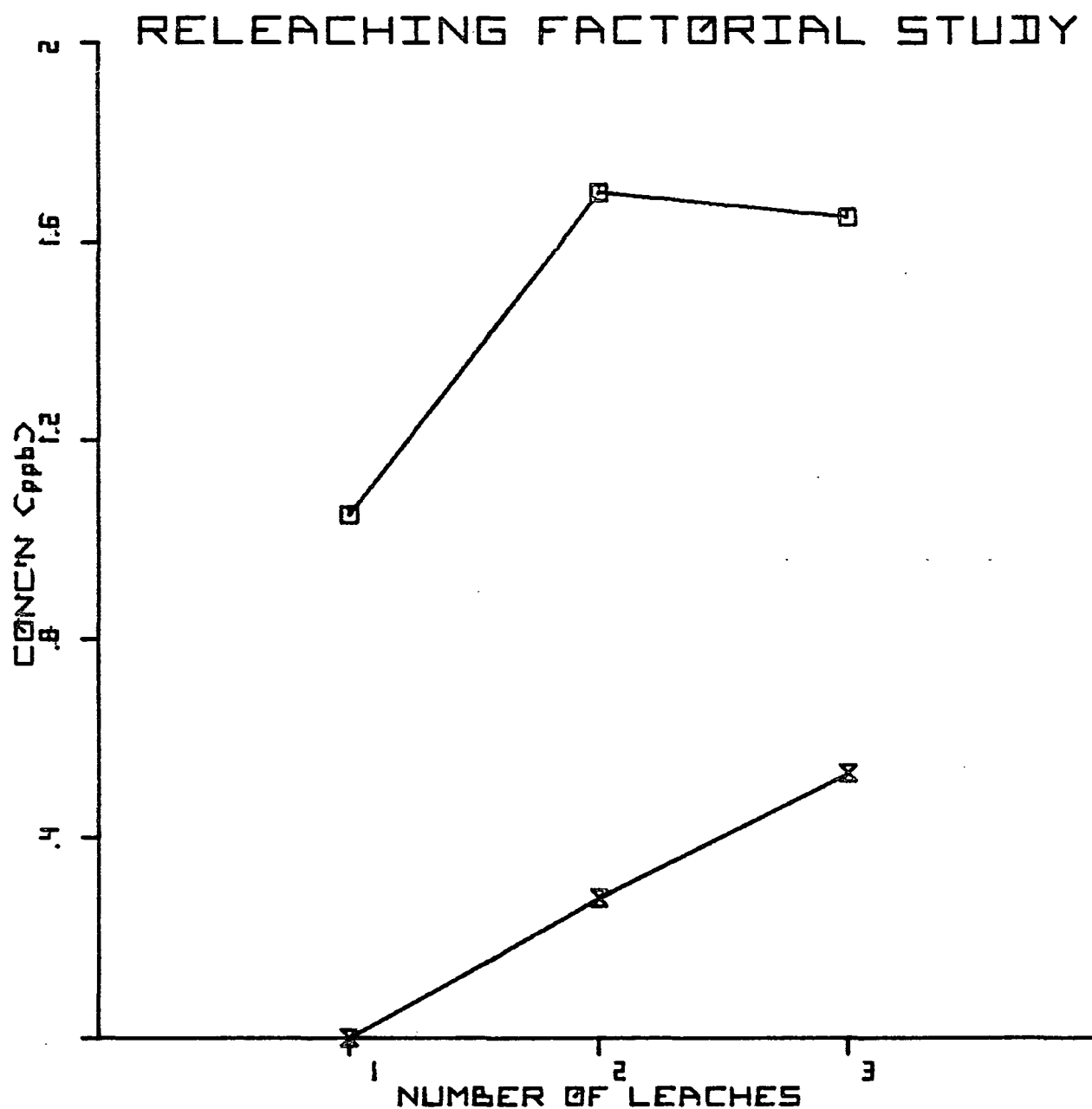X = NITROGEN SATURATION VALUES

127

FIGURE V-D-47: NICKEL
WESTERN COAL NO. 2 (0.25-0.50 mm)
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO (0.2 g/1.0 g)
TOTAL RELEASE DATA
□ = OXYGEN SATURATION VALUES
x = NITROGEN SATURATION VALUES

128

FIGURE V-D-47: NICKEL
WESTERN COAL NO. 2 <0.25-0.50 mm>
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO <0.2 g/1.0 g>
TOTAL RELEASE DATA
□ = OXYGEN SATURATION VALUES
✗ = NITROGEN SATURATION VALUES

128
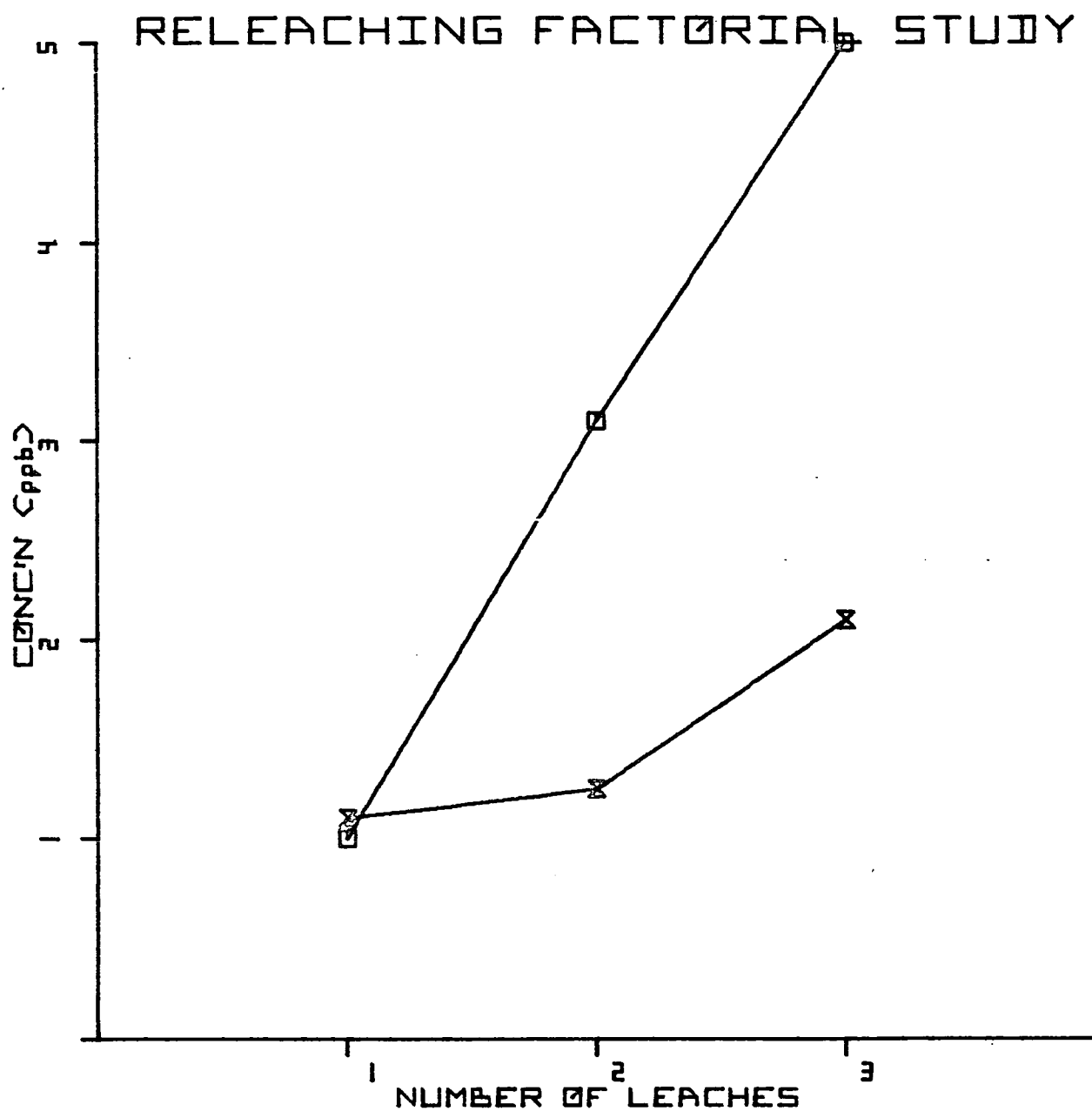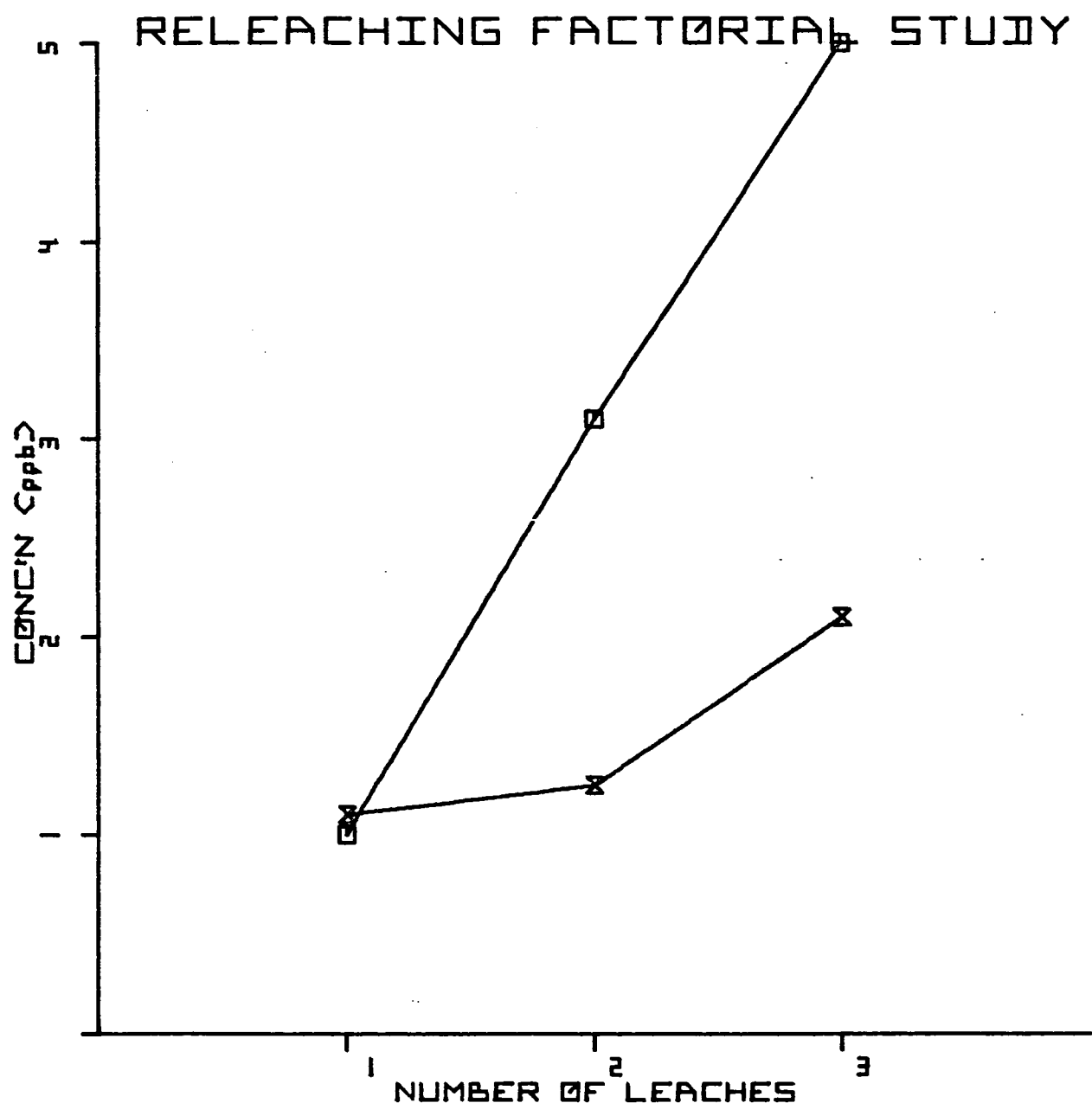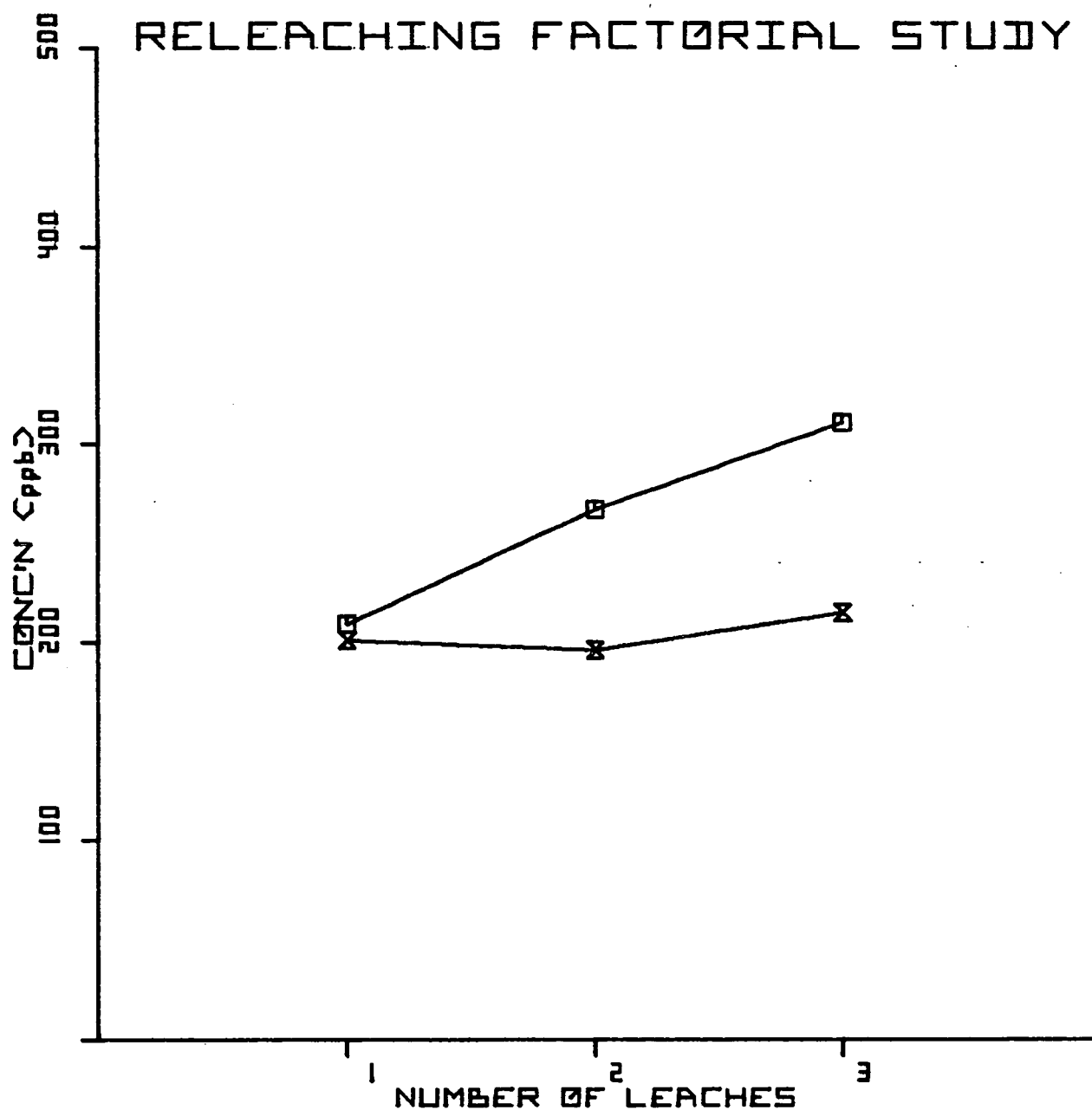
FIGURE V-D-48: NICKEL
EASTERN COAL (0.25-0.50 mm)
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO (0.2 g/1.0 g)
TOTAL RELEASE DATA
▣ = OXYGEN SATURATION VALUES
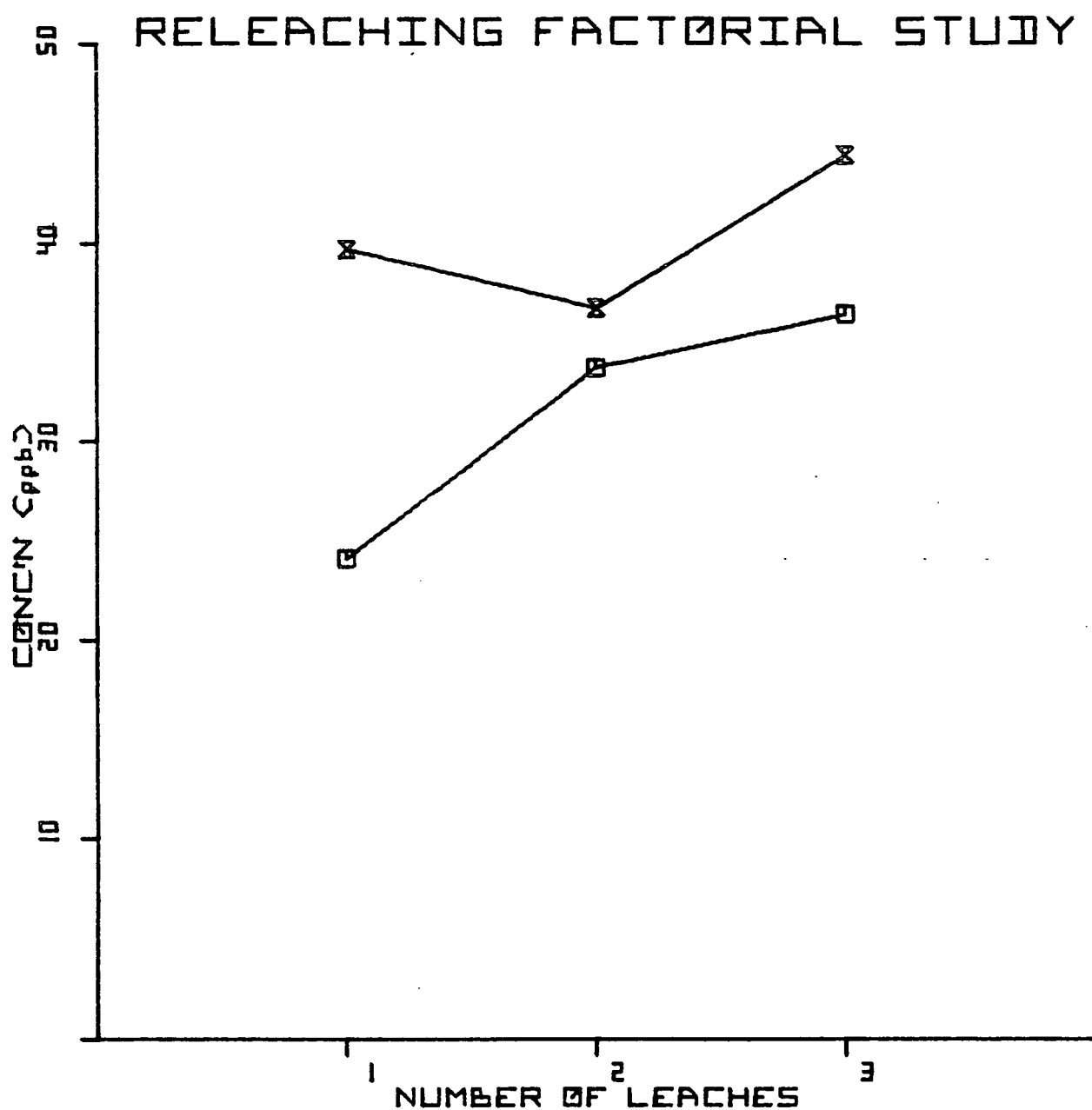✗ = NITROGEN SATURATION VALUES

129
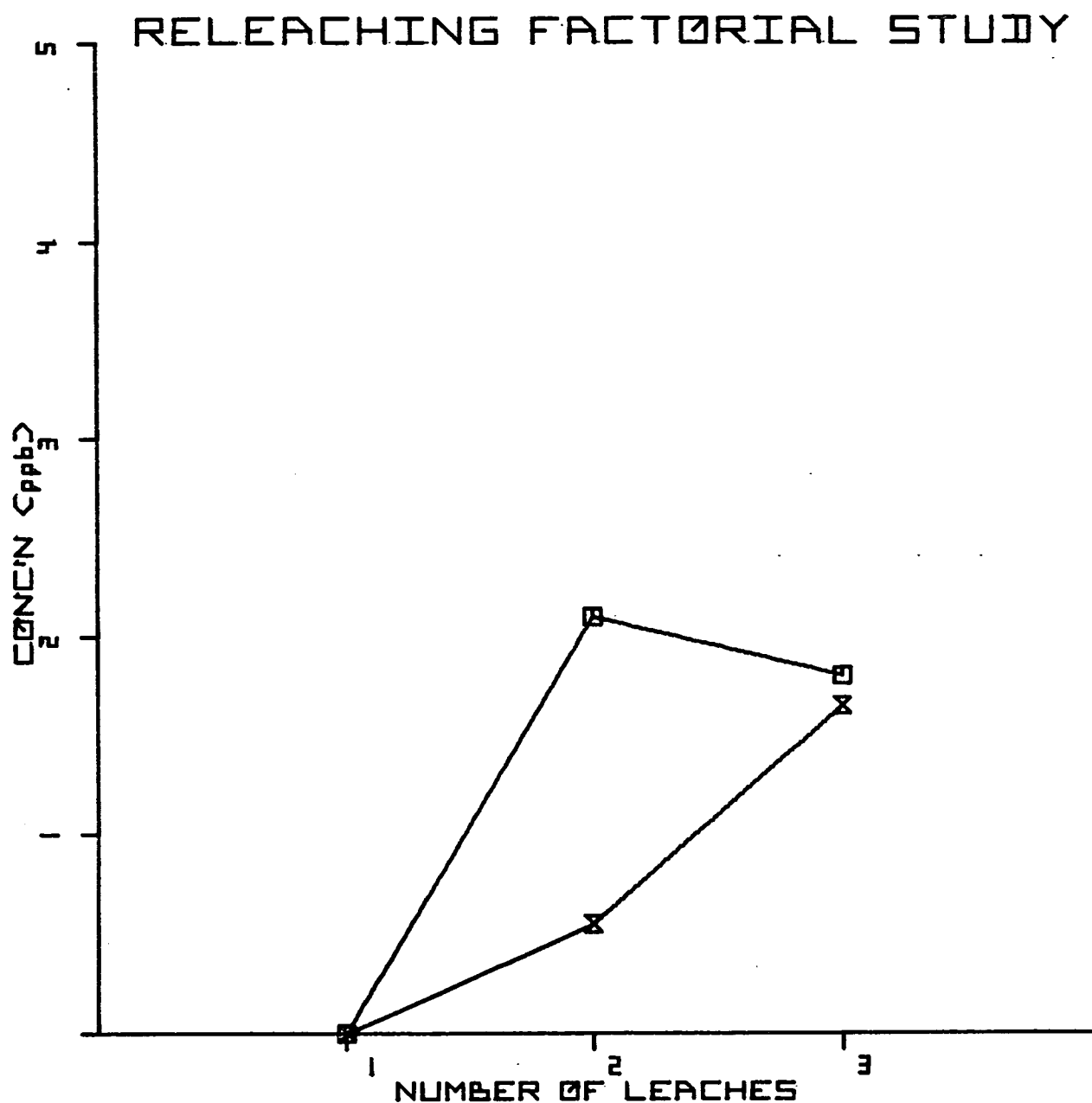
FIGURE V-D-49: SELENIUM
EASTERN COAL (0.25-0.50 mm)
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO (0.2 g/1.0 g)
TOTAL RELEASE DATA
▣ = OXYGEN SATURATION VALUES
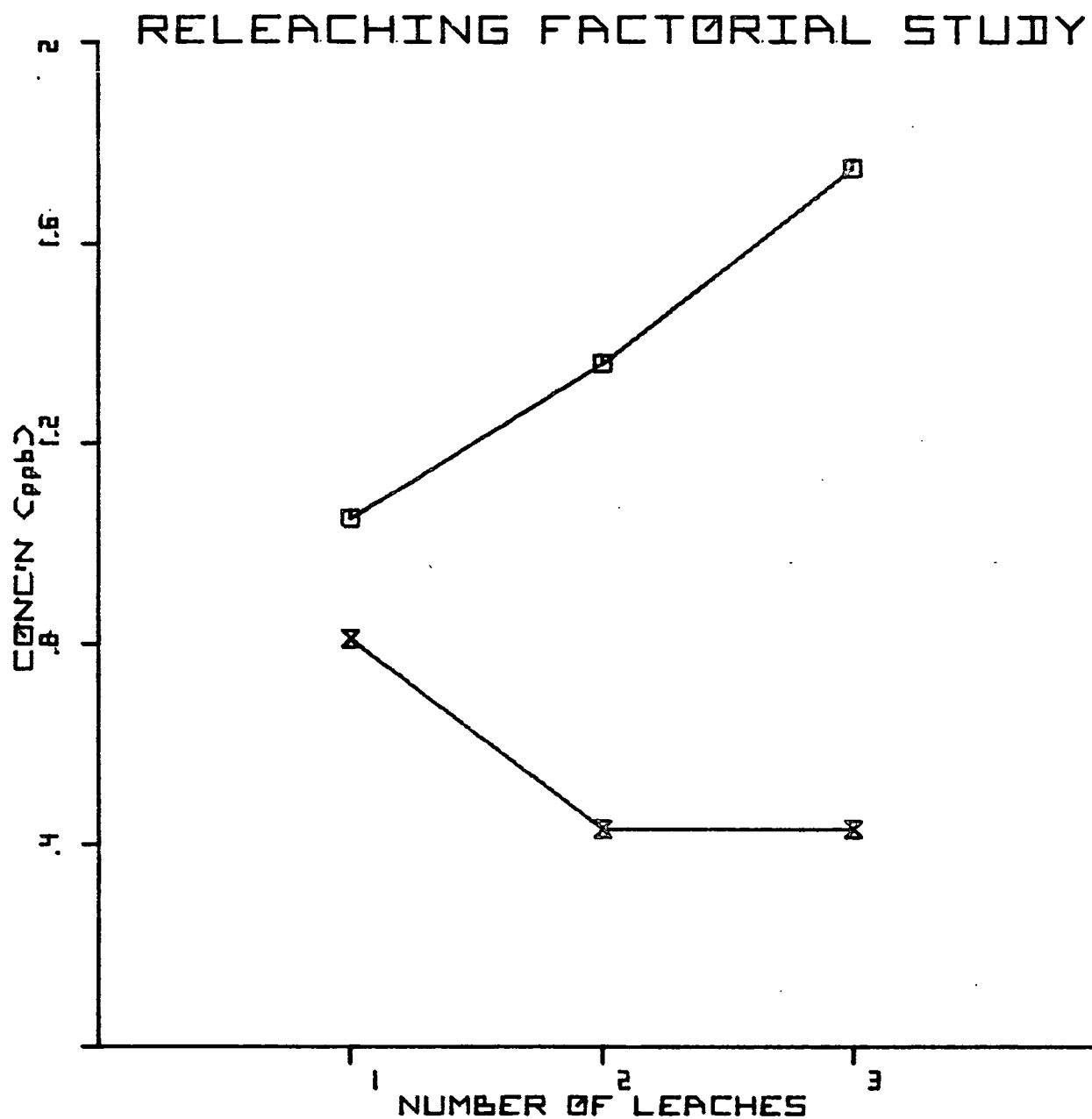✕ = NITROGEN SATURATION VALUES
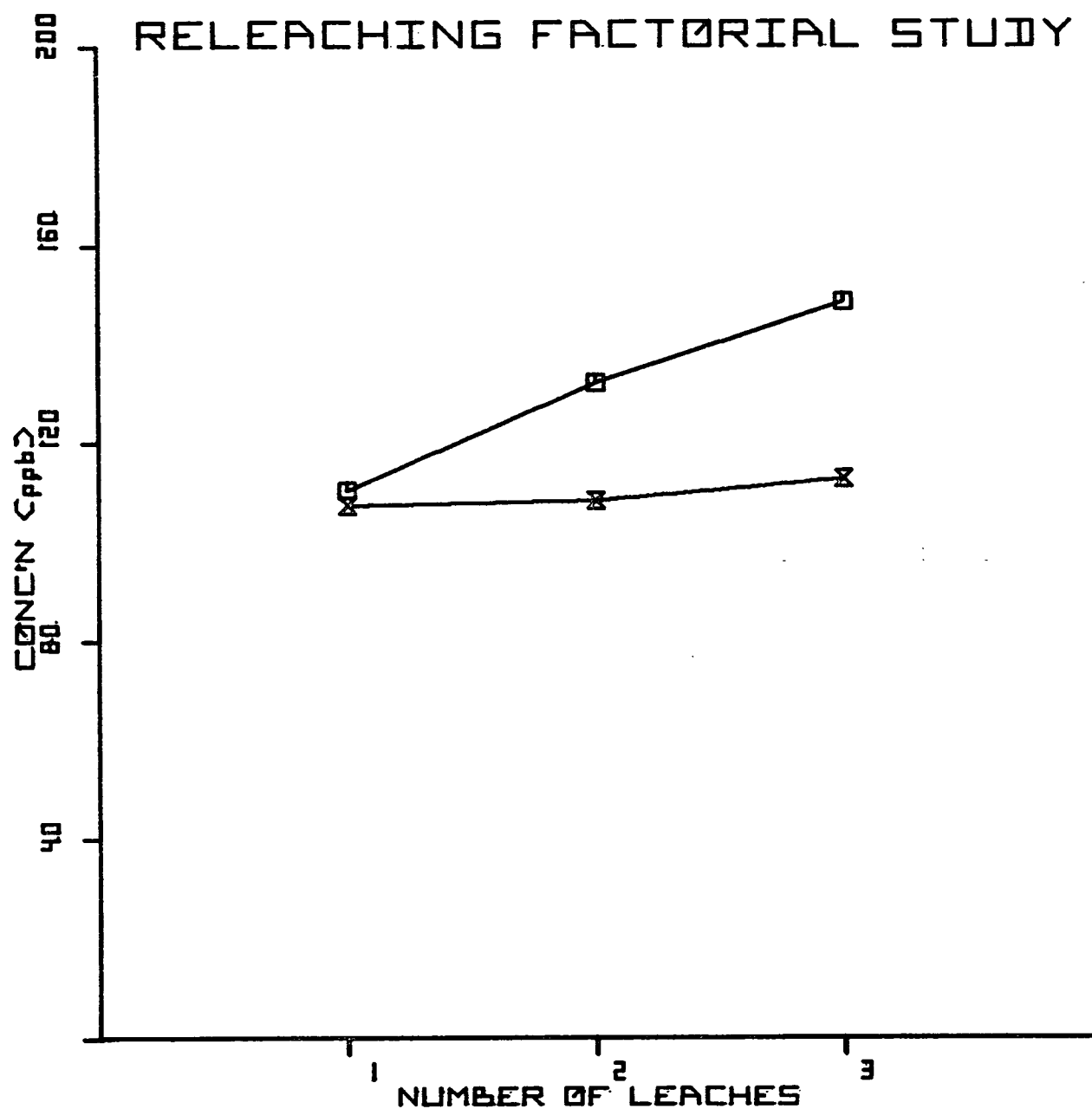
130

# RELEACHING FACTORIAL STUDY
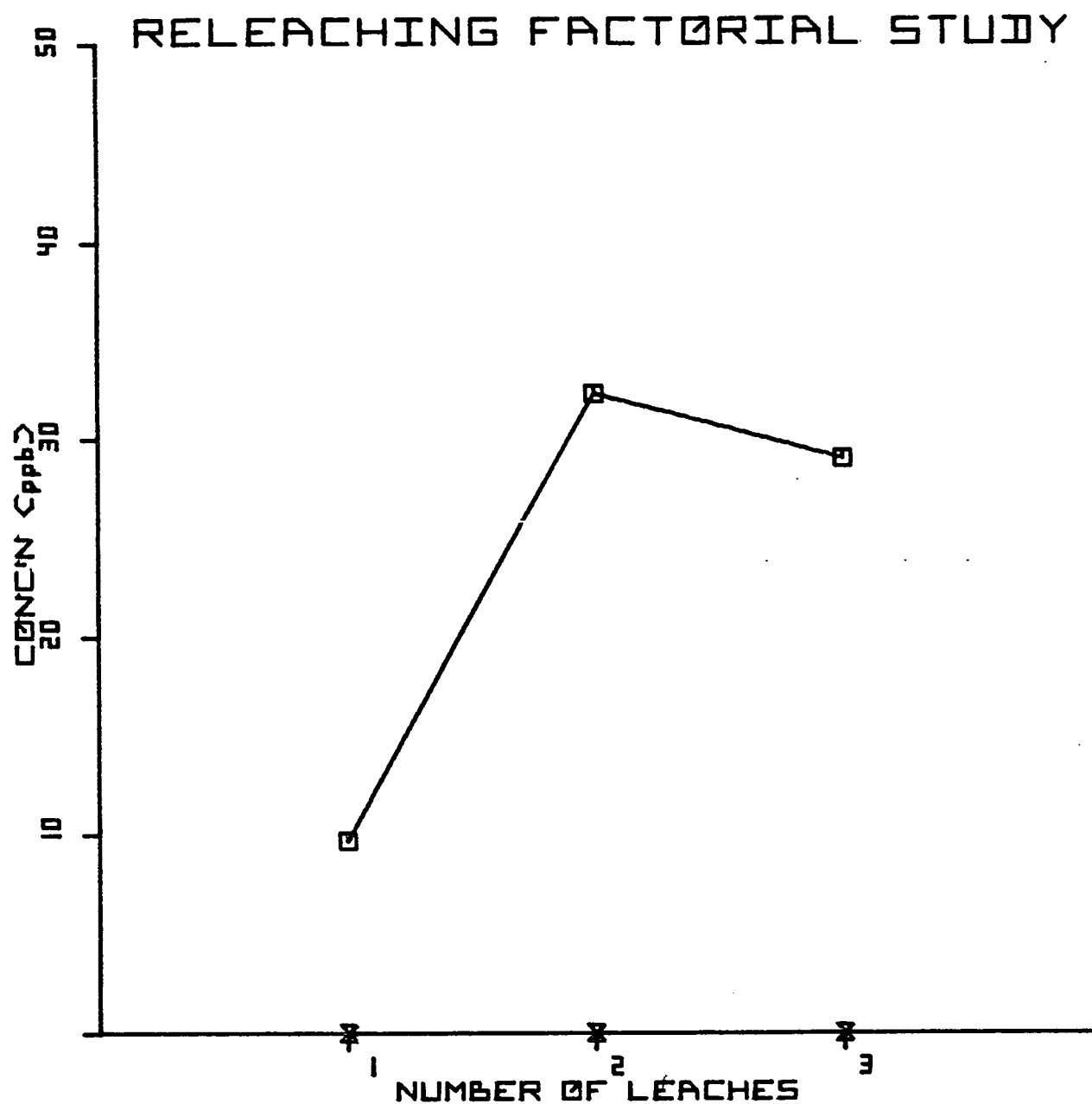


FIGURE V-D-50: VANADIUM
WESTERN COAL NO. 2 <0.25-0.50 mm>
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO <0.2 g/1.0 g>
TOTAL RELEASE DATA
◻ = OXYGEN SATURATION VALUES
✗ = NITROGEN SATURATION VALUES

131

RELEACHING FACTORIAL STUDY
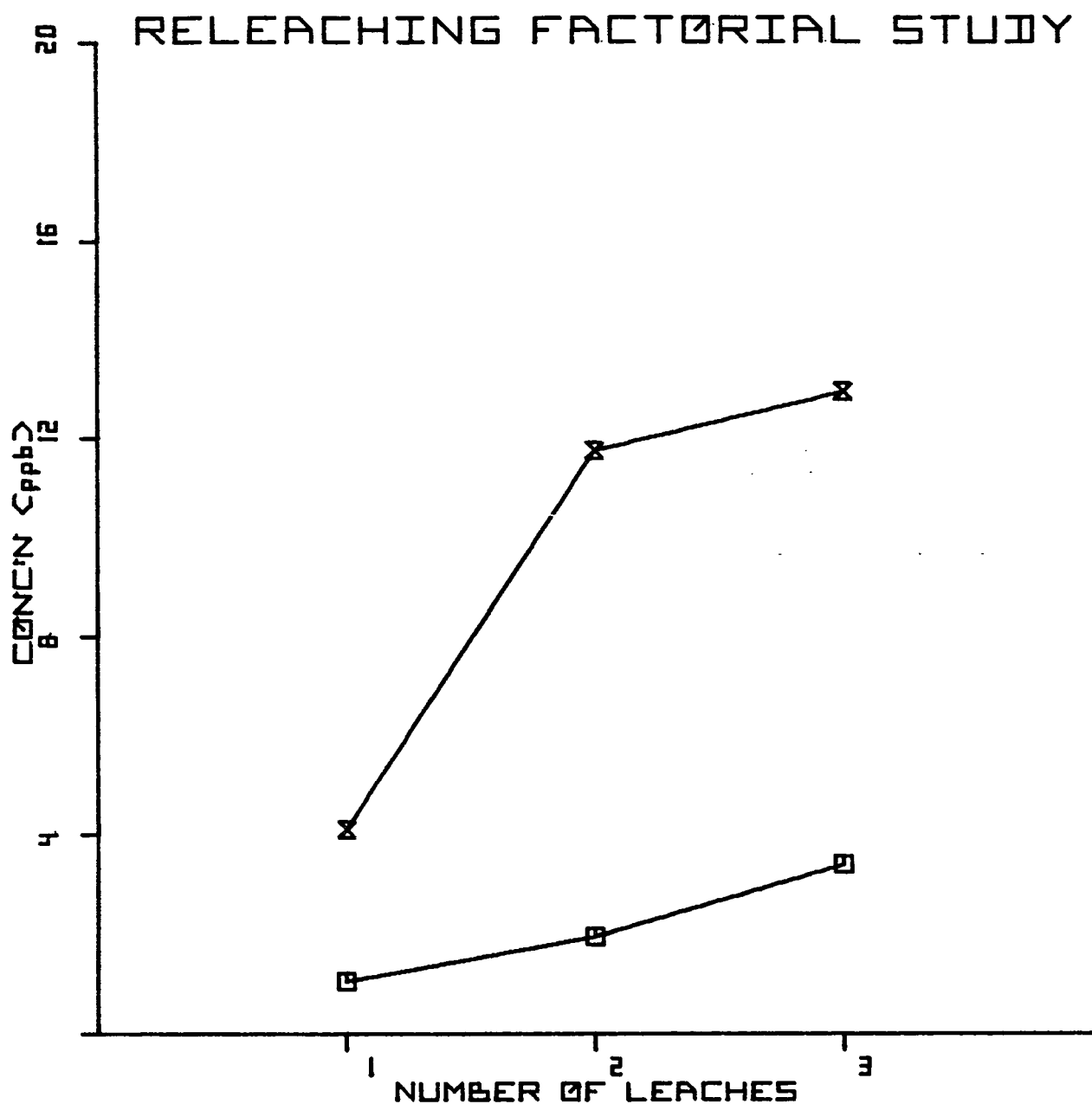
FIGURE V-D-51: ZINC
WESTERN COAL NO. 2 <0.25-0.50 mm>
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO <0.2 g/1.0 g>
TOTAL RELEASE DATA
□ = OXYGEN SATURATION VALUES
X = NITROGEN SATURATION VALUES

132

## 5. Spiked System Uptake Study

a. Experimental--

The purpose of this phase of the investigation was to determine the manner in which the total system (coal, system walls, leachant) interacted with each other in the absorption and/or release of metal ions which had been found to be present in the coal.

A "standard" coal leachate was prepared by placing 150 grams of Western Coal No. 2 and 750 ml of deionized water in a 1000 ml polypropylene bottle and shaking the mixture at similar agitation conditions to other shaker operations, as previously described, for a period of 64 hours. The leachate was then decanted from the coal, filtered and refiltered through 0.45 micron membrane filters. The "standard" leachate was then spiked to higher metal concentration levels by adding additional material from the standard solution which was prepared from the stock solutions of metals. Spiking amounts of metals in the "standard spiking" solution are listed in Table V-D-18.

TABLE V-D-18.  STANDARD SPIKING CONCENTRATIONS

| Metal | Concentration (ppb) | Metal | Concentration (ppb) |
|---|---|---|---|
| Arsenic | 2 | Manganese | 20 |
| Barium | 100 | Molybdenum | 20 |
| Cadmium | 2 | Nickel | 20 |
| Chromium | 10 | Selenium | 2 |
| Cobalt | 10 | Vanadium | 50 |
| Copper | 10 | Zinc | 10 |
| Lead | 5 | | |

Three different solutions were circulated through the continuous flow leaching apparatus. The solutions were:
1. Deionized Water (3 spiking levels)
2. Lake Superior Water (2 spiking levels)
3. Prepared Leachate (5 spiking levels)

In addition, prepared leachate at two spiking levels were circulated in the apparatus in the presence of additional coal. Coal/leachate ratio was 200 grams of coal to 1000 ml of leachant.

Also, in order to test system interactions, 250 ml leachate alone, and 250 ml leachate with 7.5 grams of small pieces of silicone tubing were shaken

in polypropylene bottles in the mechanical shaker bath to determine if possible interactions with silicone rubber tubing were a significant factor in this study. Leachant spiking levels appear in Table V-D-19.

TABLE V-D-19. LEACHANT SPIKING LEVELS

| Leachant | | Nominal Spiking Level | Leachant | Nominal Spiking Level |
|---|---|---|---|---|
| Deionized Water | | 3 X | | 0 X |
| | | 9 X | | 1 X |
| Lake Water | | 3 X | Prepared Leachate | 3 X |
| | | 9 X | | 9 X |
| | | | | 27 X |
| Polypropylene Bottles in Shaker | Leachate Alone | 0 X | Leachate and Coal | 0 X |
| | | 1 X | | 1 X |
| | Leachate and Silicone Tubing | 0 X | X = "Standard" Spiking Concentrations as Listed in Table V-D-18 | |
| | | 0 X | | |

The fluids were circulated through the system for a total of 48 hours. Samples were withdrawn without replacement of fluid at 6 and 24 hours periods, and the experiment was sampled and terminated at 48 hours. In the shaker portion of the study, contact time was also 48 hours.

All samples except those from the deionized water runs were filtered through 0.45 micron membrane filters and then stabilized with nitric acid.

Initial and final pH values were also determined.

b. Results and Discussion--
The results of the spiked system uptake study are presented in Tables V-D-20 through V-D-32. The prepared leachate 3 X* run is rejected from further consideration because (a) it shows a reverse pH effect and (b) the results are in complete disagreement with the other runs for many of the metals.

Consider first the system uptake from spiked, deionized water. Having no buffer capacity, these runs had a fairly large pH drop, probably due to atmospheric carbon dioxide. Consequently, comparisons with the other runs are probably not significant.

134

In order to get a better visualization of the various metal uptakes, Table V-D-33 has been constructed. Here, an "uptake ratio" equal to the initial concentration divided by the 48 hour concentration has been listed for each metal at 3 X and 9 X for the three systems of interest. A large value of the uptake ratio signifies a large portion of the metal absorbed by the system and lost to analysis.

In the lake water and prepared leachate systems, the metal losses would be due either to adsorption on the system walls or loss in final filtration. The final filtration loss could be due either to an adsorption on the filter or the coagulation of particles which would be retained by the filter. No systematic attempt was made to separate these effects in this work.

In the coal plus leachate system, any losses in addition to the above should be due to direct sequestering by the coal itself.

The first fact to be derived from Table V-D-33 is that a highly significant amount of metal ion is usually absorbed by the coal, and significant amounts of metal are lost to the system in most cases. A rough estimate of losses to the walls and/or final filter at pH ≅ 7.3 would be from zero to about 60% except for lead and cadmium where these losses are much larger. A study to separate the wall and filter effects at slightly basic pH values would seem to have a highly priority in any future work.

It appears that an equilibrium is established between the various parts of the system and that in a real leaching situation, the absorptive property of the coal itself is almost always the controlling factor. If one compares this section of the study with the releaching work, the coal titration studies and the EDTA experiments, the following picture emerges: Any single pass of metal free, aqueous leachant through western coal should quickly assume a pH slightly above 7.0 and will transfer some metals from the coal. The concentrations of these metals should be well below current EPA limits. Continuous leaching using continuously supplied fresh leachant would add much larger amounts of heavy metals to the environment.

135

TABLE V-D-20

SPIKED SYSTEM UPTAKE STUDY

ARSENIC

Nominal Spiking Level: X = 2 ppb

| Leaching System | Concentration | Nominal Spiking Level | Measured Initial Concentration (ppb) | Initial pH | Sample Concentrations (ppb) | | | 48 hr Sample pH |
|---|---|---|---|---|---|---|---|---|
| | | | | | 6 hr | 24 hr | 48 hr | |
| Continuous Flow Leaching Columns | Deionized Water | 3 X | 15 | 7.66 | 18 | 18 | 21 | 5.87 |
| | | 9 X | 63 | 7.62 | 42 | 48 | 40 | 5.69 |
| | Lake Water | 3 X | 12 | 7.64 | 12 | 12 | 13 | 7.50 |
| | | 9 X | 35 | 7.68 | 30 | 25 | 35 | 7.56 |
| | Prepared Leachate | 0 X | 0 | 7.60 | 0 | 0 | 0 | 7.21 |
| | | 1 X | 4.0 | 7.64 | 1.5 | 1.5 | 3.0 | 7.34 |
| | | 3 X* | 8.5 | 7.62 | 9.5 | 8.5 | 10.0 | 7.80 |
| | | 3 X | 8.5 | 7.62 | 6.0 | 8.0 | 8.0 | 7.55 |
| | | 9 X | 40 | 7.57 | 30 | 40 | 30 | 6.98 |
| | | 27 X | 110 | 7.64 | 90 | 90 | 110 | 6.92 |
| | Leachate Plus Coal | 3 X | 11.0 | 7.48 | 5.5 | 1.5 | 2.0 | 6.99 |
| | | 9 X | 40 | 7.58 | 20 | 7.5 | 5.5 | 6.81 |
| Polypropylene Bottles in Shaker Bath | Leachate | 0 X | 1.0 | 7.41 | ---- | ---- | 0.5 | ---- |
| | | 1 X | 3.0 | 7.49 | ---- | ---- | 3.5 | ---- |
| | Leachate Plus Silicone Tubing | 0 X | 1.0 | 7.41 | ---- | ---- | 0.0 | 7.20 |
| | | 1 X | 3.0 | 7.49 | ---- | ---- | 3.0 | 7.17 |

*This run probably contaminated; data is inconsistent and not used in interpretation.

## TABLE V-D-21
### SPIKED SYSTEM UPTAKE STUDY
#### BARIUM
Nominal Spiking Level:  X = 100 ppb

| Leaching System | Concentration | Nominal Spiking Level | Measured Initial Concentration (ppb) | Initial pH | Sample Concentrations (ppb) 6 hr | 24 hr | 48 hr | 48 hr Sample pH |
|---|---|---|---|---|---|---|---|---|
| Continuous Flow Leaching Columns | Deionized Water | 3 X | 240 | 7.66 | 260 | 280 | 305 | 5.87 |
| | | 9 X | 790 | 7.62 | 850 | 850 | 900 | 5.69 |
| | Lake Water | 3 X | 400 | 7.64 | 400 | 450 | 450 | 7.50 |
| | | 9 X | ---- | 7.68 | ---- | ---- | ---- | 7.56 |
| | Prepared Leachate | 0 X | 6 | 7.60 | 2 | 2 | 2 | 7.21 |
| | | 1 X | 100 | 7.64 | 70 | 35 | 30 | 7.34 |
| | | 3 X* | 240 | 7.62 | 35 | 15 | 12 | 7.80 |
| | | 3 X | 240 | 7.62 | 100 | 110 | 75 | 7.55 |
| | | 9 X | 870 | 7.57 | 620 | 470 | 450 | 6.98 |
| | | 27 X | 2570 | 7.64 | 690 | 400 | 330 | 6.92 |
| | Leachate Plus Coal | 3 X | 340 | 7.48 | 15 | 16 | 18 | 6.99 |
| | | 9 X | 1300 | 7.58 | 80 | 65 | 75 | 6.81 |
| Polypropylene Bottles in Shaker Bath | Leachate | 0 X | 7 | 7.41 | ---- | ---- | 5 | ---- |
| | | 1 X | 140 | 7.49 | ---- | ---- | 95 | ---- |
| | Leachate Plus Silicone Tubing | 0 X | 7 | 7.41 | ---- | ---- | 5 | 7.20 |
| | | 1 X | 140 | 7.49 | ---- | ---- | 95 | 7.17 |

*This run probably contaminated; data is inconsistent and not used in interpretation.

TABLE V-D-22

SPIKED SYSTEM ⬤ TAKE STUDY

CADMIUM

Nominal Spiking Level:  X =  2 ppb

| Leaching System | Concentration | Nominal Spiking Level | Measured Initial Concentration (ppb) | Initial pH | Sample Concentrations (ppb) | | | 48 hr Sample pH |
|---|---|---|---|---|---|---|---|---|
| | | | | | 6 hr | 24 hr | 48 hr | |
| Continuous | Deionized | 3 X | 5.0 | 7.66 | 5.3 | 5.0 | 6.1 | 5.87 |
| Flow | Water | 9 X | 15.4 | 7.62 | 14.1 | 12.7 | 15.4 | 5.69 |
| Leaching | Lake | 3 X | 3.6 | 7.64 | 3.0 | 2.5 | 2.2 | 7.50 |
| Columns | Water | 9 X | 14.0 | 7.68 | 11.0 | 7.0 | 6.0 | 7.56 |
| | Prepared | 0 X | 0 | 7.60 | 0.0 | 0.1 | 1.5 | 7.21 |
| | | 1 X | 1.3 | 7.64 | 0.2 | 0.2 | 1.5 | 7.34 |
| | | 3 X* | 4.9 | 7.62 | 0.3 | 0.1 | 0.0 | 7.80 |
| | Leachate | 3 X | 4.9 | 7.62 | 0.7 | 0.4 | 0.4 | 7.55 |
| | | 9 X | 10.8 | 7.57 | 4.6 | 2.0 | 3.7 | 6.98 |
| | | 27 X | 65 | 7.64 | 7.0 | 0.8 | 3.3 | 6.92 |
| | Leachate | 3 X | 3.4 | 7.48 | 0 | 0 | 0 | 6.99 |
| | Plus Coal | 9 X | 11.5 | 7.58 | 0 | 0 | 0.1 | 6.81 |
| Polypropylene | Leachate | 0 X | 0.8 | 7.41 | ---- | ---- | 0 | ---- |
| Bottles | | 1 X | 2.2 | 7.49 | ---- | ---- | 0.9 | ---- |
| in Shaker | Leachate Plus | 0 X | 0.8 | 7.41 | ---- | ---- | 0 | 7.20 |
| Bath | Silicone Tubing | 1 X | 2.2 | 7.49 | ---- | ---- | 0.9 | 7.17 |

*This run probably contaminated; data is inconsistent and not used in interpretation.

TABLE V-D-23

SPIKED SYSTEM UPTAKE STUDY

CHROMIUM

Nominal Spiking Level: X = 10 ppb

| Leaching System | Concentration | Nominal Spiking Level | Measured Initial Concentration (ppb) | Initial pH | Sample Concentrations (ppb) | | | 48 hr Sample pH |
|---|---|---|---|---|---|---|---|---|
| | | | | | 6 hr | 24 hr | 48 hr | |
| Continuous Flow Leaching Columns | Deionized Water | 3 X | 24 | 7.66 | 19 | 18 | 17 | 5.87 |
| | | 9 X | 90 | 7.62 | 60 | 55 | 50 | 5.69 |
| | Lake Water | 3 X | 25 | 7.64 | 25 | 20 | 20 | 7.50 |
| | | 9 X | 95 | 7.68 | 85 | 45 | 40 | 7.56 |
| | Prepared Leachate | 0 X | 0.1 | 7.60 | 0.0 | 0.3 | 0.0 | 7.21 |
| | | 1 X | 12.9 | 7.64 | 6.7 | 5.4 | 6.5 | 7.34 |
| | | 3 X* | 31 | 7.62 | 30 | 23 | 25 | 7.80 |
| | | 3 X | 31 | 7.62 | 25 | 23 | 21 | 7.55 |
| | | 9 X | 80 | 7.57 | 65 | 55 | 55 | 6.98 |
| | | 27 X | 290 | 7.64 | 270 | 190 | 230 | 6.92 |
| | Leachate Plus Coal | 3 X | 29 | 7.48 | 9.1 | 2.7 | 0.9 | 6.99 |
| | | 9 X | 85 | 7.58 | 29 | 2.2 | 0.9 | 6.81 |
| Polypropylene Bottles in Shaker Bath | Leachate | 0 X | 0.1 | 7.41 | ---- | ---- | 0.1 | ---- |
| | | 1 X | 8.5 | 7.49 | ---- | ---- | 8.4 | ---- |
| | Leachate Plus Silicone Tubing | 0 X | 0.1 | 7.41 | ---- | ---- | 0.1 | 7.20 |
| | | 1 X | 8.5 | 7.49 | ---- | ---- | 8.3 | 7.17 |

*This run probably contaminated; data is inconsistent and not used in interpretation.

TABLE V-D-24

SPIKED SYSTEM UPTAKE STUDY

COBALT

Nominal Spiking Level: X = 10 ppb

| Leaching System | Concentration | Nominal Spiking Level | Measured Initial Concentration (ppb) | Initial pH | Sample Concentrations (ppb) | | | 48 hr Sample pH |
|---|---|---|---|---|---|---|---|---|
| | | | | | 6 hr | 24 hr | 48 hr | |
| Continuous | Deionized | 3 X | 23 | 7.66 | 23 | 24 | 27 | 5.87 |
| | Water | 9 X | 90 | 7.62 | 90 | 90 | 90 | 5.69 |
| Flow | Lake | 3 X | 27 | 7.64 | 28 | 22 | 27 | 7.50 |
| Leaching | Water | 9 X | 100 | 7.68 | 90 | 75 | 65 | 7.56 |
| Columns | | 0 X | 0 | 7.60 | 0 | 0 | 0 | 7.21 |
| | Prepared | 1 X | 8.8 | 7.64 | 3.2 | 1.7 | 1.2 | 7.34 |
| | | 3 X* | 30 | 7.62 | 5.2 | 2.5 | 1.4 | 7.80 |
| | Leachate | 3 X | 30 | 7.62 | 13.7 | 12.0 | 10.6 | 7.55 |
| | | 9 X | 90 | 7.57 | 65 | 45 | 45 | 6.98 |
| | | 27 X | 320 | 7.64 | 120 | 70 | 30 | 6.92 |
| | Leachate | 3 X | 27 | 7.48 | 0 | 0 | 0 | 6.99 |
| | Plus Coal | 9 X | 105 | 7.58 | 1.7 | 1.1 | 0.9 | 6.81 |
| Polypropylene | Leachate | 0 X | 0 | 7.41 | ---- | ---- | 0 | ---- |
| Bottles | | 1 X | 7.8 | 7.49 | ---- | ---- | 8.5 | ---- |
| in Shaker | Leachate Plus | 0 X | 0 | 7.41 | ---- | ---- | 0 | 7.20 |
| Bath | Silicone Tubing | 1 X | 7.8 | 7.49 | ---- | ---- | 8.4 | 7.17 |

*This run probably contaminated; data is inconsistent and not used in interpretation.

TABLE V-D-25
SPIKED SYSTEM UPTAKE STUDY

COPPER

Nominal Spiking Level: X = 10 ppb

| Leaching System | Concentration | Nominal Spiking Level | Measured Initial Concentration (ppb) | Initial pH | Sample Concentrations (ppb) | | | 48 hr Sample pH |
|---|---|---|---|---|---|---|---|---|
| | | | | | 6 hr | 24 hr | 48 hr | |
| Continuous Flow Leaching Columns | Deionized Water | 3 X | 18 | 7.66 | 23 | 22 | 23 | 5.87 |
| | | 9 X | 75 | 7.62 | 70 | 70 | 70 | 5.69 |
| | Lake Water | 3 X | 30 | 7.64 | 18 | 19 | 13 | 7.50 |
| | | 9 X | 85 | 7.68 | 50 | 25 | 10 | 7.56 |
| | Prepared Leachate | 0 X | 2.5 | 7.60 | 0.5 | 5.5 | 1.3 | 7.21 |
| | | 1 X | 10 | 7.64 | 3.0 | 6.5 | 4.2 | 7.34 |
| | | 3 X* | 26 | 7.62 | 4.0 | 8.0 | 4.0 | 7.80 |
| | | 3 X | 26 | 7.62 | 11 | 10 | 10 | 7.55 |
| | | 9 X | 80 | 7.57 | 35 | 25 | 20 | 6.98 |
| | | 27 X | 245 | 7.64 | 65 | 20 | 10 | 6.92 |
| | Leachate Plus Coal | 3 X | 27 | 7.48 | 6.0 | ·5.0 | 3.0 | 6.99 |
| | | 9 X | 95 | 7.58 | 5.0 | 4.0 | 3.0 | 6.81 |
| Polypropylene Bottles in Shaker Bath | Leachate | 0 X | 1.0 | 7.41 | ---- | ---- | 2.0 | ---- |
| | | 1 X | 11 | 7.49 | ---- | ---- | 6.0 | ---- |
| | Leachate Plus Silicone Tubing | 0 X | 1.0 | 7.41 | ---- | ---- | 4.0 | 7.20 |
| | | 1 X | 11 | 7.49 | ---- | ---- | 13 | 7.17 |

*This run probably contaminated; data is inconsistent and not used in interpretation.

141

TABLE V-D-26

SPIKED SYSTEM UPTAKE STUDY

<u>LEAD</u>

Nominal Spiking Level:  X =  5 ppb

| Leaching System | Concentration | Nominal Spiking Level | Measured Initial Concentration (ppb) | Initial pH | Sample Concentrations (ppb) | | | 48 hr Sample pH |
|---|---|---|---|---|---|---|---|---|
| | | | | | 6 hr | 24 hr | 48 hr | |
| Continuous Flow Leaching Columns | Deionized Water | 3 X | 8.0 | 7.66 | 7.0 | 7.4 | 8.1 | 5.87 |
| | | 9 X | 30 | 7.62 | 19 | 19 | 21 | 5.69 |
| | Lake Water | 3 X | 7.8 | 7.64 | 5.0 | 4.6 | 2.3 | 7.50 |
| | | 9 X | 30 | 7.68 | 20 | 2.0 | 0.9 | 7.56 |
| | Prepared Leachate | 0 X | 0 | 7.60 | 0 | 0 | 0 | 7.21 |
| | | 1 X | 1.6 | 7.64 | 0.2 | 0.0 | 0.1 | 7.34 |
| | | 3 X* | 7.1 | 7.62 | 0.6 | 2.3 | 0.2 | 7.80 |
| | | 3 X | 7.1 | 7.62 | 0.7 | 0.3 | 0.3 | 7.55 |
| | | 9 X | 30 | 7.57 | 8.0 | 3.0 | 1.9 | 6.98 |
| | | 27 X | 80 | 7.64 | 60 | 30 | 25 | 6.92 |
| | Leachate Plus Coal | 3 X | 8.0 | 7.48 | 0.5 | 0.2 | 0.2 | 6.99 |
| | | 9 X | 25 | 7.58 | 0.0 | 0.2 | 0.1 | 6.81 |
| Polypropylene Bottles in Shaker Bath | Leachate | 0 X | 0.1 | 7.41 | ---- | ---- | 0.3 | ---- |
| | | 1 X | 2.5 | 7.49 | ---- | ---- | 1.5 | ---- |
| | Leachate Plus Silicone Tubing | 0 X | 0.1 | 7.41 | ---- | ---- | 0.3 | 7.20 |
| | | 1 X | 2.5 | 7.49 | ---- | ---- | 1.2 | 7.17 |

*This run probably contaminated; data is inconsistent and not used in interpretation.

142

TABLE V-D-27

SPIKED SYSTEM UPTAKE STUDY

MANGANESE

Nominal Spiking Level:  X =  20 ppb

| Leaching System | Concentration | Nominal Spiking Level | Measured Initial Concentration (ppb) | Initial pH | Sample Concentrations (ppb) | | | 48 hr Sample pH |
|---|---|---|---|---|---|---|---|---|
| | | | | | 6 hr | 24 hr | 48 hr | |
| Continuous | Deionized | 3 X | 50 | 7.66 | 45 | 47 | 50 | 5.87 |
| | Water | 9 X | 150 | 7.62 | 135 | 130 | 145 | 5.69 |
| Flow | Lake | 3 X | 60 | 7.64 | 47 | 60 | 38 | 7.50 |
| Leaching | Water | 9 X | 150 | 7.68 | 140 | 107 | 95 | 7.56 |
| Columns | | 0 X | 0.7 | 7.60 | 0.1 | 0.6 | 0.1 | 7.21 |
| | Prepared | 1 X | 18.3 | 7.64 | 5.6 | 3.8 | 3.4 | 7.34 |
| | | 3 X* | 50 | 7.62 | 11.1 | 4.6 | 2.4 | 7.80 |
| | Leachate | 3 X | 50 | 7.62 | 27 | 17.2 | 18.1 | 7.55 |
| | | 9 X | 150 | 7.57 | 105 | 85 | 80 | 6.98 |
| | | 27 X | 470 | 7.64 | 230 | 100 | 60 | 6.92 |
| | Leachate | 3 X | 55 | 7.48 | 0.4 | 0.4 | 0.3 | 6.99 |
| | Plus Coal | 9 X | 195 | 7.58 | 5.5 | 2.2 | 2.3 | 6.81 |
| Polypropylene | Leachate | 0 X | 0.8 | 7.41 | ---- | ---- | 0.5 | ---- |
| Bottles | | 1 X | 18.4 | 7.49 | ---- | ---- | 15.2 | ---- |
| in Shaker | Leachate Plus | 0 X | 0.8 | 7.41 | ---- | ---- | 0.3 | 7.20 |
| Bath | Silicone Tubing | 1 X | 18.4 | 7.49 | ---- | ---- | 16.4 | 7.17 |

*This run probably contaminated; data is inconsistent and not used in interpretation.

143

## TABLE V-D-28
## SPIKED SYSTEM UPTAKE STUDY
### MOLYBDENUM
#### Nominal Spiking Level:  X = 20 ppb

| Leaching System | Concentration | Nominal Spiking Level | Measured Initial Concentration (ppb) | Initial pH | Sample Concentrations (ppb) 6 hr | 24 hr | 48 hr | 48 hr Sample pH |
|---|---|---|---|---|---|---|---|---|
| Continuous Flow Leaching Columns | Deionized Water | 3 X | 50 | 7.66 | 50 | 55 | 60 | 5.87 |
| | | 9 X | 180 | 7.62 | 160 | 180 | 150 | 5.69 |
| | Lake Water | 3 X | 105 | 7.64 | 105 | 100 | 100 | 7.50 |
| | | 9 X | 200 | 7.68 | 250 | 240 | 210 | 7.56 |
| | Prepared Leachate | 0 X | 0 | 7.60 | 0 | 0 | 0 | 7.21 |
| | | 1 X | 12 | 7.64 | 12 | 9 | 11 | 7.34 |
| | | 3 X* | 60 | 7.62 | 35 | 45 | 50 | 7.80 |
| | | 3 X | 60 | 7.62 | 45 | 45 | 50 | 7.55 |
| | | 9 X | 120 | 7.57 | 150 | 120 | 160 | 6.98 |
| | | 27 X | 530 | 7.64 | 540 | 430 | 490 | 6.92 |
| | Leachate Plus Coal | 3 X | 63 | 7.48 | 40 | 42 | 40 | 6.99 |
| | | 9 X | 160 | 7.58 | 130 | 110 | 100 | 6.81 |
| Polypropylene Bottles in Shaker Bath | Leachate | 0 X | 0.4 | 7.41 | ---- | ---- | 0.0 | ---- |
| | | 1 X | 11.1 | 7.49 | ---- | ---- | 9.2 | ---- |
| | Leachate Plus Silicone Tubing | 0 X | 0.4 | 7.41 | ---- | ---- | 0.0 | 7.20 |
| | | 1 X | 11.1 | 7.49 | ---- | ---- | 9.2 | 7.17 |

*This run probably contaminated; data is inconsistent and not used in interpretation.

144

TABLE V-D-29

SPIKED SYSTEM UPTAKE STUDY

NICKEL

Nominal Spiking Level: X = 20 ppb

| Leaching System | Concentration | Nominal Spiking Level | Measured Initial Concentration (ppb) | Initial pH | Sample Concentrations (ppb) | | | 48 hr Sample pH |
|---|---|---|---|---|---|---|---|---|
| | | | | | 6 hr | 24 hr | 48 hr | |
| Continuous Flow Leaching Columns | Deionized Water | 3 X | 67 | 7.66 | 58 | 53 | 53 | 5.87 |
| | | 9 X | 170 | 7.62 | 150 | 170 | 150 | 5.69 |
| | Lake Water | 3 X | 60 | 7.64 | 47 | 60 | 38 | 7.50 |
| | | 9 X | 150 | 7.68 | 140 | 107 | 95 | 7.56 |
| | Prepared Leachate | 0 X | 1 | 7.60 | 1 | 3 | 0 | 7.21 |
| | | 1 X | 17 | 7.64 | 17 | 11 | 15 | 7.34 |
| | | 3 X* | 46 | 7.62 | 11 | 11 | 7 | 7.80 |
| | | 3 X | 46 | 7.62 | 34 | 38 | 25 | 7.55 |
| | | 9 X | 210 | 7.57 | 160 | 160 | 110 | 6.98 |
| | | 27 X | 600 | 7.64 | 450 | 110 | 70 | 6.92 |
| | Leachate Plus Coal | 3 X | 46 | 7.48 | 3 | 2 | 4 | 6.99 |
| | | 9 X | 170 | 7.58 | 9 | 3 | 4 | 6.81 |
| Polypropylene Bottles in Shaker Bath | Leachate | 0 X | 1 | 7.41 | ---- | ---- | 1 | ---- |
| | | 1 X | 17 | 7.49 | ---- | ---- | 19 | ---- |
| | Leachate Plus Silicone Tubing | 0 X | 1 | 7.41 | ---- | ---- | 3 | 7.20 |
| | | 1 X | 17 | 7.49 | ---- | ---- | 17 | 7.17 |

*This run probably contaminated; data is inconsistent and not used in interpretation.

TABLE V-D-30
SPIKED SYSTEM UPTAKE STUDY
SELENIUM

Nominal Spiking Level: X = 2 ppb

| Leaching System | Concentration | Nominal Spiking Level | Measured Initial Concentration (ppb) | Initial pH | Sample Concentrations (ppb) | | | 48 hr Sample pH |
|---|---|---|---|---|---|---|---|---|
| | | | | | 6 hr | 24 hr | 48 hr | |
| Continuous Flow Leaching Columns | Deionized Water | 3 X | 7 | 7.66 | 6 | 7 | 5 | 5.87 |
| | | 9 X | 20 | 7.62 | 20 | 19 | 20 | 5.69 |
| | Lake Water | 3 X | 9 | 7.64 | 6 | 9 | 8 | 7.50 |
| | | 9 X | 19 | 7.68 | 20 | 21 | 20 | 7.56 |
| | Prepared Leachate | 0 X | 0 | 7.60 | 0 | 0 | 0 | 7.21 |
| | | 1 X | 2 | 7.64 | 2 | 0 | 2 | 7.34 |
| | | 3 X* | 6 | 7.62 | 6 | 5 | 3 | 7.80 |
| | | 3 X | 6 | 7.62 | 6 | 5 | 3 | 7.55 |
| | | 9 X | 19 | 7.57 | 14 | 16 | 14 | 6.98 |
| | | 27 X | 60 | 7.64 | 60 | 60 | 50 | 6.92 |
| | Leachate Plus Coal | 3 X | 8 | 7.48 | 6 | 5 | 0 | 6.99 |
| | | 9 X | 21 | 7.58 | 13 | 4 | 2 | 6.81 |
| Polypropylene Bottles in Shaker Bath | Leachate | 0 X | 0 | 7.41 | ---- | ---- | 0 | ---- |
| | | 1 X | 3 | 7.49 | ---- | ---- | 0 | ---- |
| | Leachate Plus Silicone Tubing | 0 X | 0 | 7.41 | ---- | ---- | 0 | 7.20 |
| | | 1 X | 3 | 7.49 | ---- | ---- | 2 | 7.17 |

*This run probably contaminated; data is inconsistent and not used in interpretation.

TABLE V-D-31
SPIKED SYSTEM UPTAKE STUDY

VANADIUM

Nominal Spiking Level: X = 50 ppb

| Leaching System | Concentration | Nominal Spiking Level | Measured Initial Concentration (ppb) | Initial pH | Sample Concentrations (ppb) | | | 48 hr Sample pH |
|---|---|---|---|---|---|---|---|---|
| | | | | | 6 hr | 24 hr | 48 hr | |
| Continuous Flow Leaching Columns | Deionized Water | 3 X | 190 | 7.66 | 150 | 150 | 190 | 5.87 |
| | | 9 X | 750 | 7.62 | 550 | 700 | 650 | 5.69 |
| | Lake Water | 3 X | 240 | 7.64 | 210 | 230 | 250 | 7.50 |
| | | 9 X | 650 | 7.68 | 850 | 650 | 700 | 7.56 |
| | Prepared Leachate | 0 X | 3 | 7.60 | 0 | 0 | 0 | 7.21 |
| | | 1 X | 80 | 7.64 | 45 | 25 | 30 | 7.34 |
| | | 3 X* | 200 | 7.62 | 160 | 190 | 160 | 7.80 |
| | | 3 X | 200 | 7.62 | 160 | 180 | 180 | 7.55 |
| | | 9 X | 750 | 7.57 | 550 | 600 | 600 | 6.98 |
| | | 27 X | 2200 | 7.64 | 1900 | 1650 | 1800 | 6.92 |
| | Leachate Plus Coal | 3 X | 240 | 7.48 | 70 | 30 | 15 | 6.99 |
| | | 9 X | 850 | 7.58 | 150 | 70 | 35 | 6.81 |
| Polypropylene Bottles in Shaker Bath | Leachate | 0 X | 0 | 7.41 | ---- | ---- | 0 | ---- |
| | | 1 X | 70 | 7.49 | ---- | ---- | 85 | ---- |
| | Leachate Plus Silicone Tubing | 0 X | 0 | 7.41 | ---- | ---- | 0 | 7.20 |
| | | 1 X | 70 | 7.49 | ---- | ---- | 85 | 7.17 |

*This run probably contaminated; data is inconsistent and not used in interpretation.

147

TABLE V-D-32

SPIKED SYSTEM UPTAKE STUDY

ZINC

Nominal Spiking Level: X = 10 ppb

| Leaching System | Concentration | Nominal Spiking Level | Measured Initial Concentration (ppb) | Initial pH | Sample Concentrations (ppb) | | | 48 hr Sample pH |
|---|---|---|---|---|---|---|---|---|
| | | | | | 6 hr | 24 hr | 48 hr | |
| Continuous Flow Leaching Columns | Deionized Water | 3 X | 15 | 7.66 | 15 | 15 | 15 | 5.87 |
| | | 9 X | 55 | 7.62 | 50 | 55 | 55 | 5.69 |
| | Lake Water | 3 X | 15 | 7.64 | 7.0 | 7.0 | 5.0 | 7.50 |
| | | 9 X | 50 | 7.68 | 40 | 20 | 20 | 7.56 |
| | Prepared Leachate | 0 X | 1.1 | 7.60 | 0.3 | 1.3 | 0.9 | 7.21 |
| | | 1 X | 8.7 | 7.64 | 1.3 | 8.2 | 1.5 | 7.34 |
| | | 3 X* | 16 | 7.62 | 4.0 | 4.2 | 3.2 | 7.80 |
| | | 3 X | 16 | 7.62 | 7.2 | 17 | 12 | 7.55 |
| | | 9 X | 55 | 7.57 | 20 | 20 | 15 | 6.98 |
| | | 27 X | 160 | 7.64 | 45 | 35 | 15 | 6.92 |
| | Leachate Plus Coal | 3 X | 22 | 7.48 | 1.4 | 1.2 | 0.9 | 6.99 |
| | | 9 X | 80 | 7.58 | 1.3 | 1.4 | 3.4 | 6.81 |
| Polypropylene Bottles in Shaker Bath | Leachate | 0 X | 1.4 | 7.41 | ---- | ---- | 1.4 | ---- |
| | | 1 X | 5.5 | 7.49 | ---- | ---- | 5.5 | ---- |
| | Leachate Plus Silicone Tubing | 0 X | 1.4 | 7.41 | ---- | ---- | 1.5 | 7.20 |
| | | 1 X | 5.5 | 7.49 | ---- | ---- | 6.2 | 7.17 |

*This run probably contaminated; data is inconsistent and not used in interpretation.

TABLE V-D-33.  UPTAKE RATIO $= \dfrac{\text{INITIAL CONCENTRATION}}{\text{FINAL CONCENTRATION}}$

| Metal | Lake Water | | Prepared Leachate | | Leachate and Coal | |
|-------|------|------|------|------|------|------|
|       | 3 X  | 9 X  | 3 X  | 9 X  | 3 X  | 9 X  |
| As | 0.92 | 1.0 | 1.1 | 1.3 | 5.5 | 7.3 |
| Ba | 0.89 | --- | 3.2 | 1.9 | 19 | 17 |
| Cd | 1.6 | 2.3 | 12 | 2.9 | ∞ | 115 |
| Cr | 1.3 | 2.4 | 1.5 | 1.5 | 32 | 94 |
| Co | 1.0 | 1.5 | 2.8 | 2.0 | ∞ | 117 |
| Cu | 2.3 | 8.5 | 2.6 | 4.0 | 9.0 | 32 |
| Pb | 3.4 | 30 | 24 | 16 | 40 | 250 |
| Mn | 1.6 | 1.6 | 2.8 | 1.9 | 183 | 85 |
| Mo | 1.1 | 0.95 | 1.2 | 0.75 | 1.6 | 1.6 |
| Ni | 1.6 | 1.6 | 1.8 | 1.9 | 12 | 43 |
| Se | 1.1 | 0.95 | 2.0 | 1.4 | ∞ | 11 |
| V | 0.96 | 0.93 | 1.1 | 1.3 | 16 | 24 |
| Zn | 3.0 | 2.5 | 1.3 | 3.7 | 24 | 24 |

149

## 6. EDTA Shaker Study

### a. Experimental--

The purpose of this study was to determine the amount of metal which was capable of being mobilized by a leachant of extremely high seqkestering power. A leachant with high sequestering ability could be capable of a more vigorous competition with complexing sites on the coal matrix and thus give an indication of the amount of metal which could ultimately be removed by very prolonged leaching with leachants of lower complexing power.

A 0.01 M solution of ethylenediaminetetraacetic acid, di-sodium salt (EDTA) was prepared using deionized water as a solvent, and the pH of the resulting EDTA solution was adjusted to an appropriate level by the use of either ultrapure nitric acid or sodium hydroxide. pH levels of 7.5 and 3.4 were used in this experiment.

These hydrogen ion concentrations were chosen because the self-buffering action of the western coals resulted in an alkaline solution when deionized water was used as a leachant, while the eastern coal sample produced a distinctly acidic system. By pre-setting the pH of the EDTA leachant, it was felt that any effect would be due to the initial sequestering ability of the leachant, rather than to self-titration of the coal-disodium EDTA mixture.

One hundred ml of the EDTA solution which had been adjusted to pH 7.5 was added to separate 20.0 gram samples of Western Coals No. 1 and No. 2.

The coal sample and EDTA solution were placed into a 125 ml polypropylene bottle. In a similar manner, 100 ml of EDTA solution (adjusted to pH 3.4) was added to 20.0 grams of eastern coal. Coal samples were in the 0.500-1.00 mm size range. All three types of samples were run in duplicate.

The coal-EDTA mixtures were placed in a constant temperature shaker bath and were allowed to shake for 48 hours at a temperature of approximately 40°C. The shaking rate was one oscillation of the sample platform per second. Sample platform travel was 28 mm.

After 48 hours, the pH of an unfiltered portion of each sample was determined and the remaining portion of the sample was filtered through a 0.45 micron membrane filter, using an all-plastic construction suction filtration apparatus. After filtration, the samples were acidified to stabilize them, and the metal concentrations were determined by flameless atomic absorption spectrophotometry.[1, 2, 11, 15, 16]

One hundred ml portions of the high and low pH adjusted EDTA solutions were shaken along with the coal-EDTA samples and used as control blanks in the analyses. All metals except mercury were determined.

### b. Results and Discussion--

The initial observation is that the EDTA-coal systems shifted pH to more acid levels. See Table V-D-34. This would, of course, be expected from reactions such as:

150

$$H_2Y^{2-} + M^{2+} \longrightarrow YM^{2-} + 2H^+$$
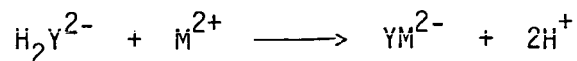
where $Y^{4-}$ is the completely ionized EDTA ion and $M^{2+}$ is any di-positive metal ion. Because the initial pH levels were set to the natural, buffered levels of coal-deionized water systems, these observed shifts demonstrate that a significant amount of EDTA complexation in taking place in the system.

The pH shift also makes interpretation of the data more difficult because of the dependence of metal leaching on pH.

The leachate analyses for the EDTA runs are shown in Table V-D-34. This table also lists analyses for comparable non-EDTA runs.

Examination of Table V-D-34 shows that EDTA extracts significantly more metal ion from the coal than pure deionized water with the exceptions of: (a) a strong reversal for cobalt in the Eastern Coal and (b) a possibly reversed value for selenium in the Western Coal No. 1. Strong evidence that the effect is not due to pH alone is given by the comparison between EDTA runs and the acetate buffered run for Western Coal No. 1. Here, the comparison run has a lower final pH than the EDTA runs and yet the metal extraction is still significantly higher for the EDTA runs than for the comparison run.

From an environmental viewpoint, it would appear that there could be significant amounts of heavy metal mobilization with strong complexing agents.

## TABLE V-D-34

### Leachate Analysis for EDTA Runs and Values for Comparable Non-EDTA Runs

| Coal | Western #1 | | | Western #2 | | Eastern | |
|---|---|---|---|---|---|---|---|
| Run Designation | Shaker Run With Water Deionized | Shaker Run With Acetate Buffer | EDTA Runs (Average of 2 Runs) | Continuous Flow Run With Water Deionized | EDTA Runs (Average of 2 Runs) | Continuous Flow Run With Water Deionized | EDTA Runs |
| Initial pH | | | 7.51 | | 7.51 | | 3.41 |
| Final pH | 7.23 | 7.74 | .5.56 | 7.48 | 6.11 | 3.31 | 2.66 |
| Metals | | | | | | | |
| As | 1.7 | 3.8 | 5.1 | 0.0 | 0.5 | 0.0 | 140 |
| Ba | 40 | 582 | 405 | 3 | 425 | 32 | 110 |
| Cd | 0.6 | 1.6 | 2.6 | 0.15 | 1.0 | 3.5 | 2.8 |
| Cr | 0.3 | 0.3 | (3.6) | 0.1 | 1.1 | 0.4 | 18 |
| Co | 0.2 | 1.1 | 19.6 | 0.0 | 10.0 | 98 | 13.7 |
| Cu | 4.2 | 3.0 | 135 | 1.5 | 70 | 5.5 | 200 |
| Pb | 0 | 0 | 62 | 0.0 | 30 | 0 | 70 |
| Mn | 1.3 | 80 | 1250 | 0.1 | 950 | 660 | 1130 |
| Mo | 0.7 | 5.1 | 4 | 0.6 | 1 | 0 | 12 |
| Ni | 5* | 5* | 65 | 0.5 | 40 | 170 | 285 |
| Se | 1 | 6 | (0.8) | 0.0 | 0.2 | 0 | 3.0 |
| V | 0 | 0 | 50 | 0.0 | 10 | 0 | 10 |
| Zn | 35 | 8 | 53 | 6 | 29 | 120 | 225 |

Values in parenthesis are doubtful because of high blanks

*Approximate values from 1st factorial run.

## 7. Short Term Shaker Study

### a. Experimental--

A short term shaker run was undertaken to determine whether or not a higher concentration of metals would be found in leachate samples which were obtained at less than two hours of contact time between leachant and coal, than from those in which samples were obtained after four or more hours of contact between leachant and coal. This experiment was performed in order to determine if there was an initial "surge" of metal from the coal, with subsequent redeposition on the coal and/or the walls of the leaching system.

Six 125 ml polypropylene bottles, each containing 15.0 grams of 0.500-1.00 mm sized Western Coal No. 2 (obtained from the ORBA transshipment facility) and 75 ml of deionized water were placed in a constant temperature shaker bath. The samples were maintained at a temperature of 40°C and were shaken gently at a cycle rate of approximately one oscillation per second for the specified lengths of time.

Samples were removed from analysis at the following times: 15 min, 30 min, 1 hr, 2 hr, 4 hr and 6 hr. After the removal of the sample bottle from the shaker bath at a designated time, a portion of the unfiltered leachate was removed for a determination of the pH of the leachate.

The remainder of the leachate was filtered with suction through a 0.45 micron member filter supported in an all-plastic filtration apparatus, and then acidified to a pH of approximately 2 with ultrapure nitric acid. The acidified, filtered leachate was preserved for metal analysis by flameless atomic absorption spectrophotometry. All metals except mercury were determined.

### b. Results and Discussion--

Of the metals analyzed, only barium, cadmium, cobalt, copper, manganese, nickel, selenium and zinc gave results at or above detection limits. The data for these metals are given in Fig. V-D-52 through V-D-59. Initial spikes seem to appear for all of the above metals. There is no adequate explanation at present for the phenomenon.

Throughout this work, metal analyses at very short times showed wild fluctuations with initial spikes. This experiment was done to confirm this effect.

The results of this experiment support the decision to accept 6 or more hours contact as a first sampling time for most of the work. The basic model for this research was a static coal pile subjected to slow, flow-through, leaching. Short term, initial fluctuations should have little effect on the longer, more equilibrium-like, metal levels.
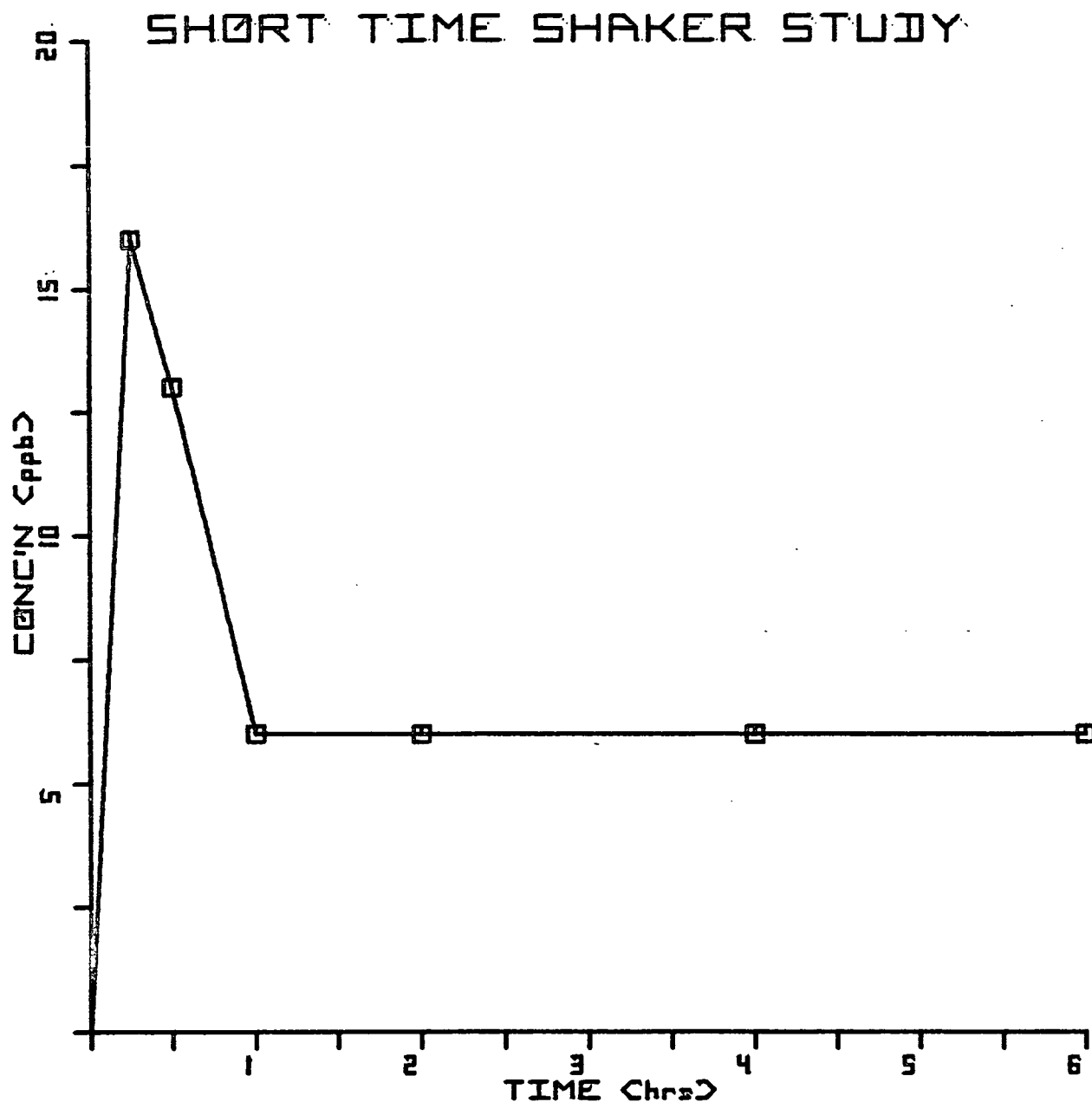
153

FIGURE V-D-52:   BARIUM
WESTERN COAL NO. 2 <0.50-1.00 MM>
DEIONIZED WATER LEACHANT
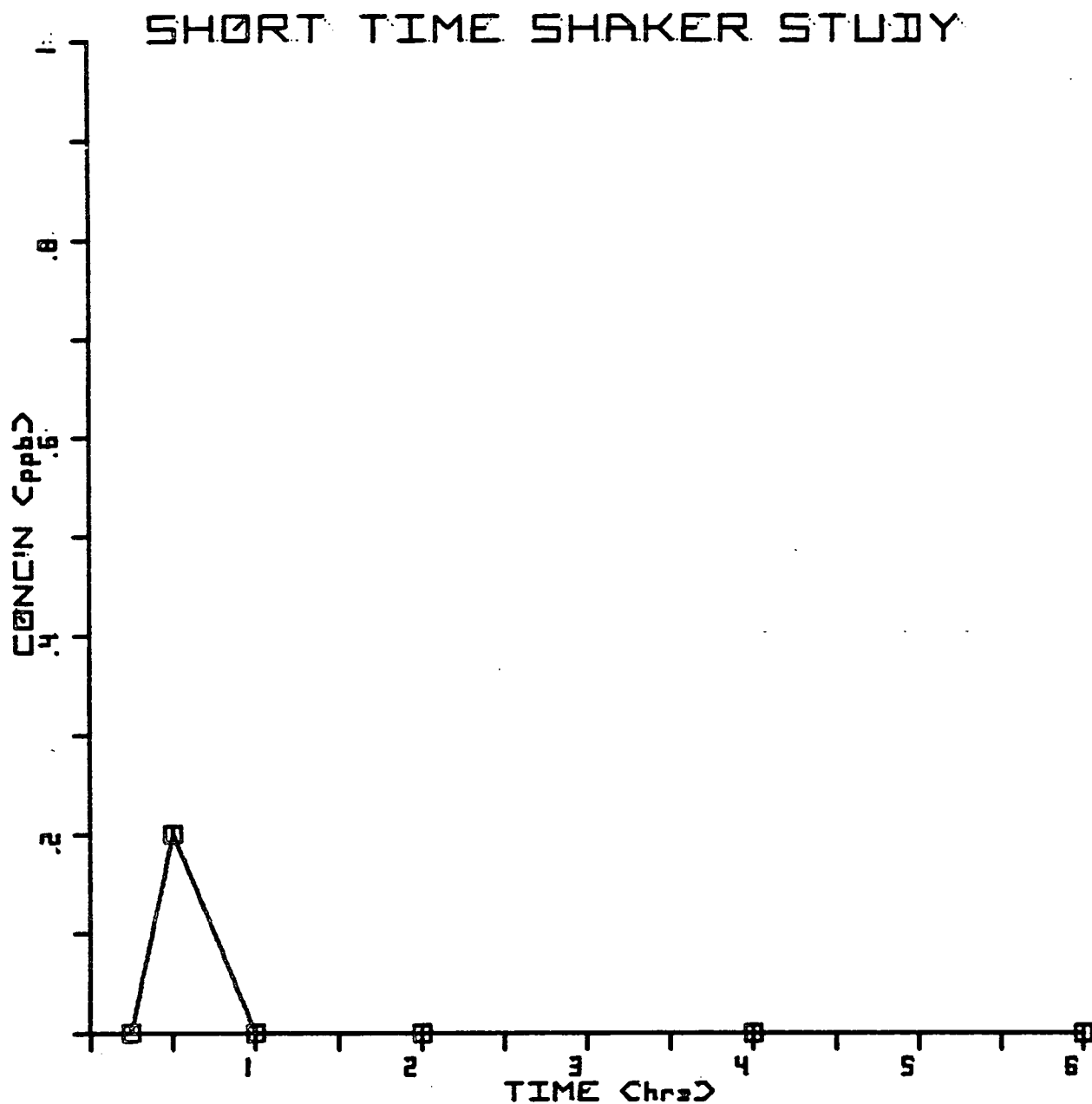COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE

FIGURE V-D-53: CADMIUM
WESTERN COAL NO. 2 (0.50-1.00 MM)
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO = 0.2 G./1.0 G
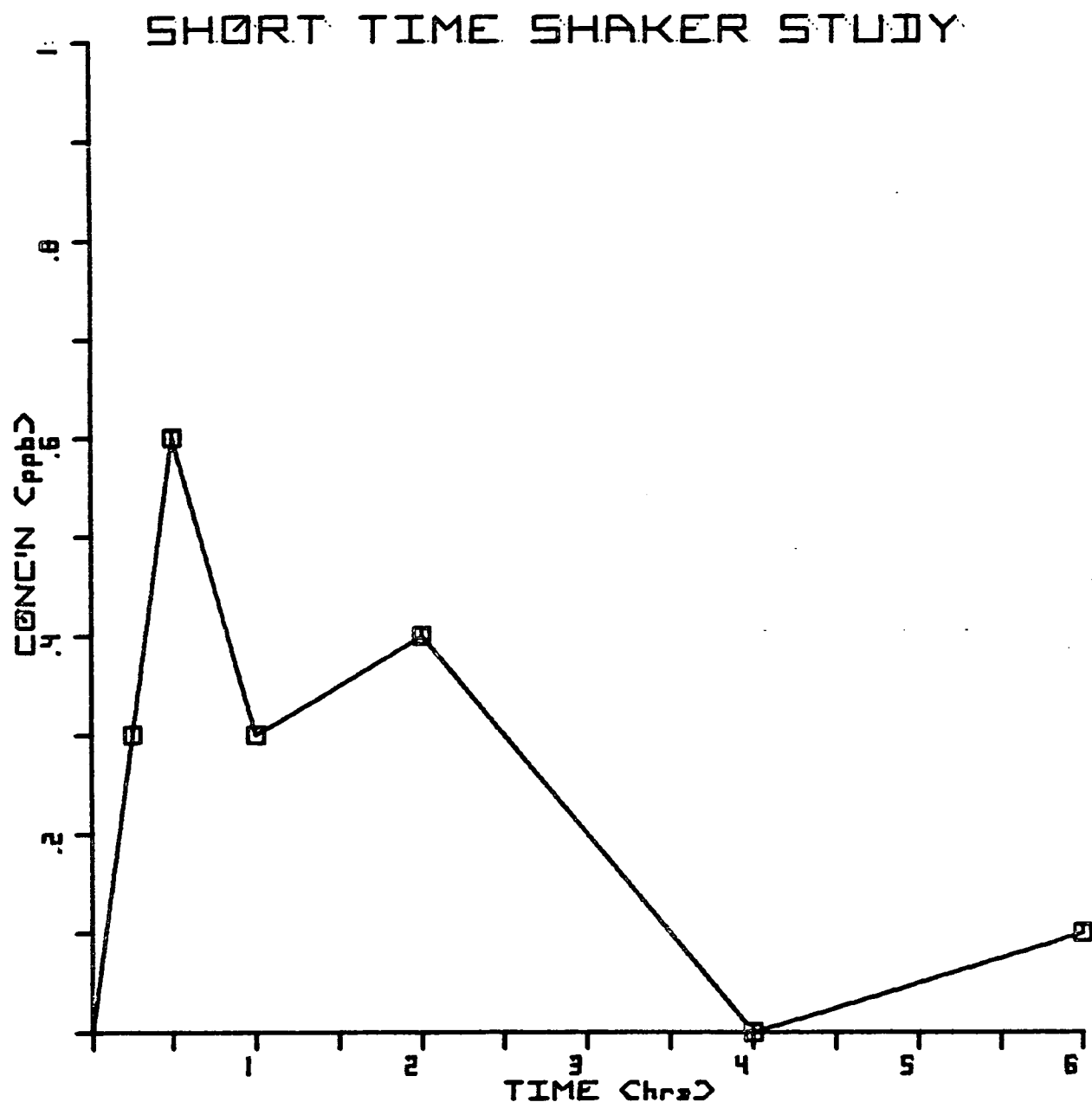AIR ATMOSPHERE
TOTAL RELEASE

SHORT TIME SHAKER STUDY

FIGURE V-D-54:     COBALT
WESTERN COAL NO. 2 (0.50-1.00 MM)
DEIONIZED WATER LEACHANT
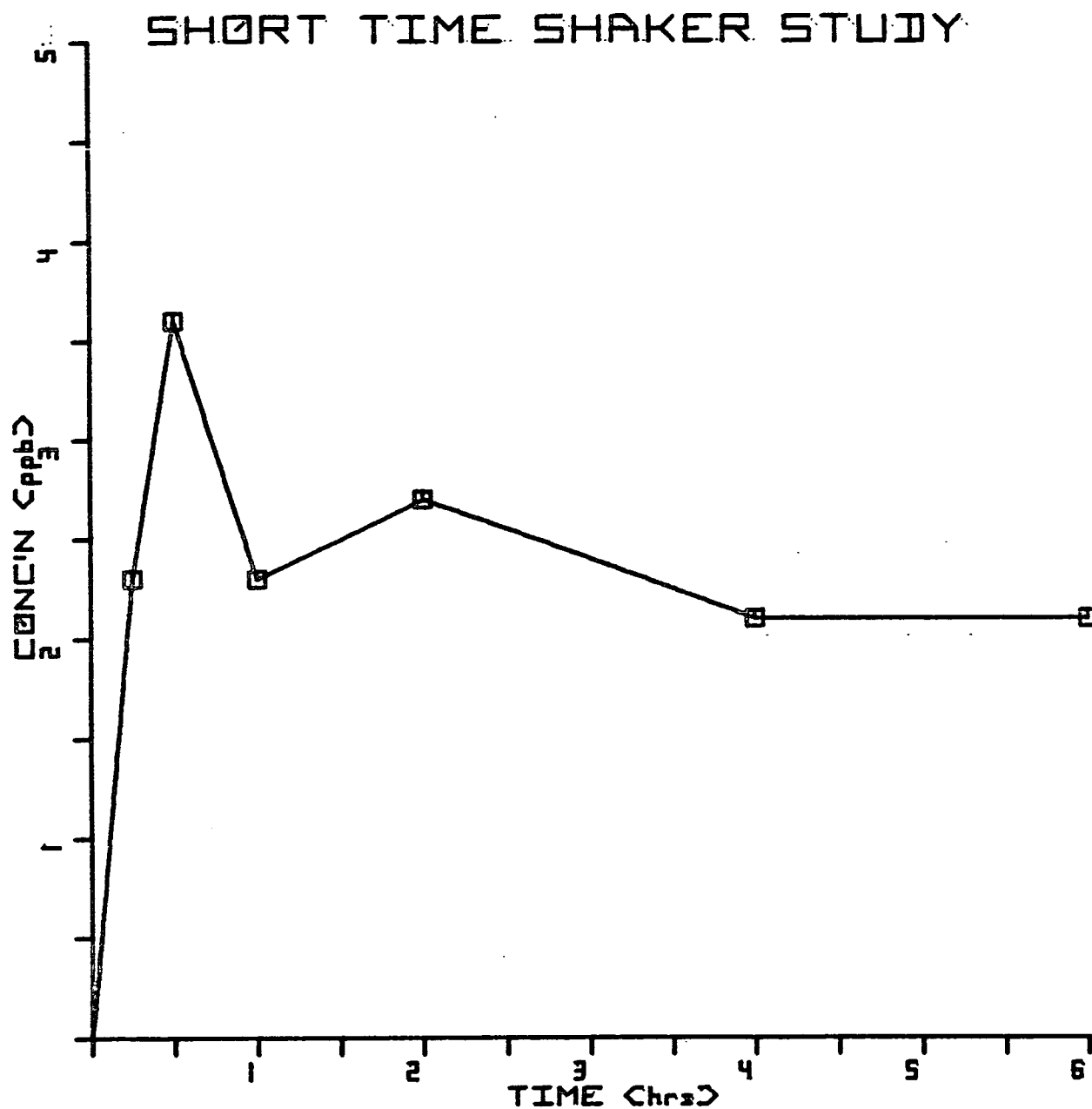COAL/LEACHANT RATIO : 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE

156

FIGURE V-D-55:    COPPER
                  WESTERN COAL NO. 2 <0.50-1.00 MM>
                  DEIONIZED WATER LEACHANT
                  COAL/LEACHANT RATIO : 0.2 G./1.0 G
                  AIR ATMOSPHERE
                  TOTAL RELEASE

# SHORT TIME SHAKER STUDY



FIGURE V-D-56:     MANGANESE
WESTERN COAL NO. 2 (0.50-1.00 MM)
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO = 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE

SHORT TIME SHAKER STUDY

FIGURE V-D-57:    NICKEL
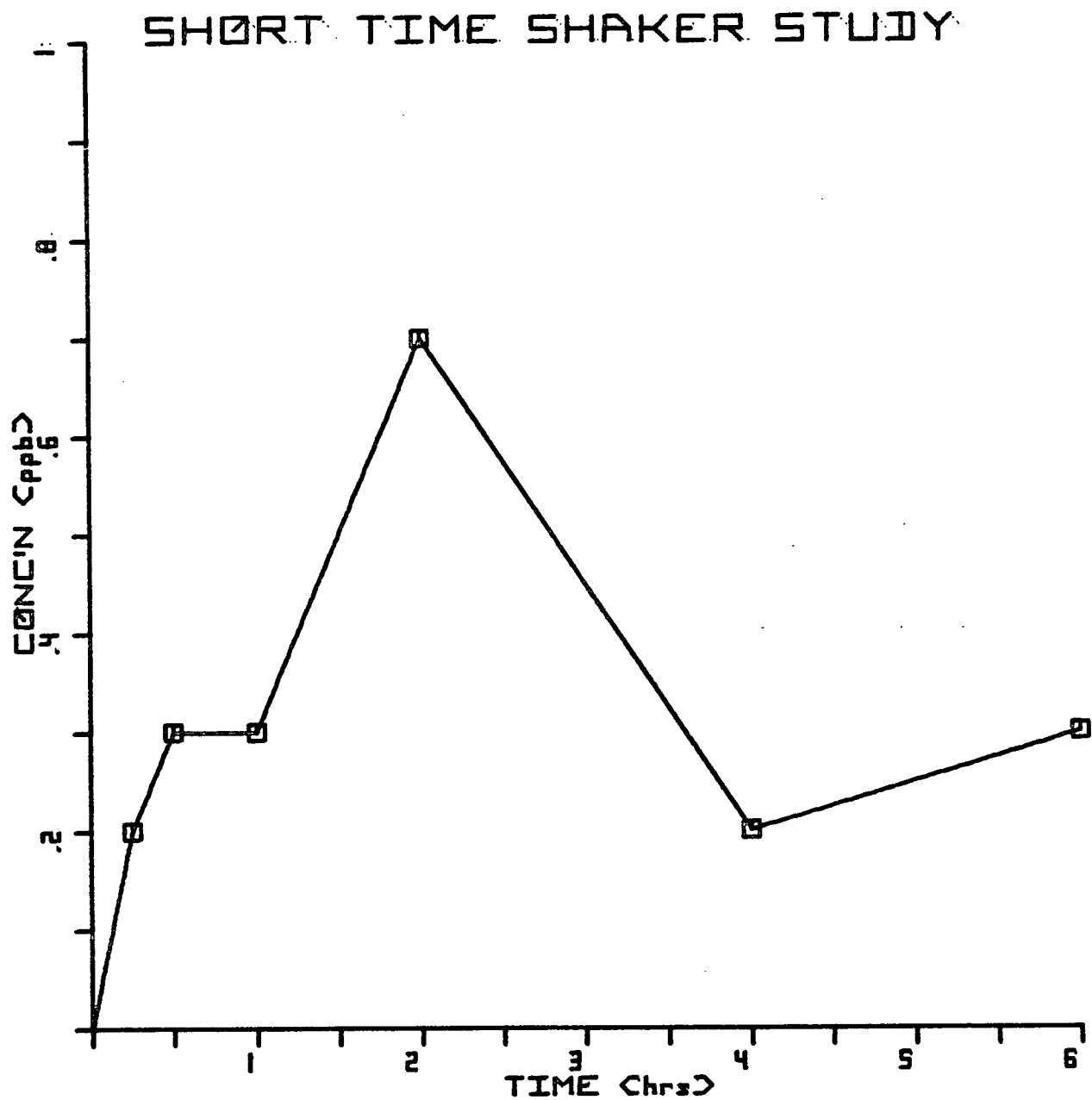                 WESTERN COAL NO. 2 <0.50-1.00 MM>
                 DEIONIZED WATER LEACHANT
                 COAL/LEACHANT RATIO : 0.2 G./1.0 G
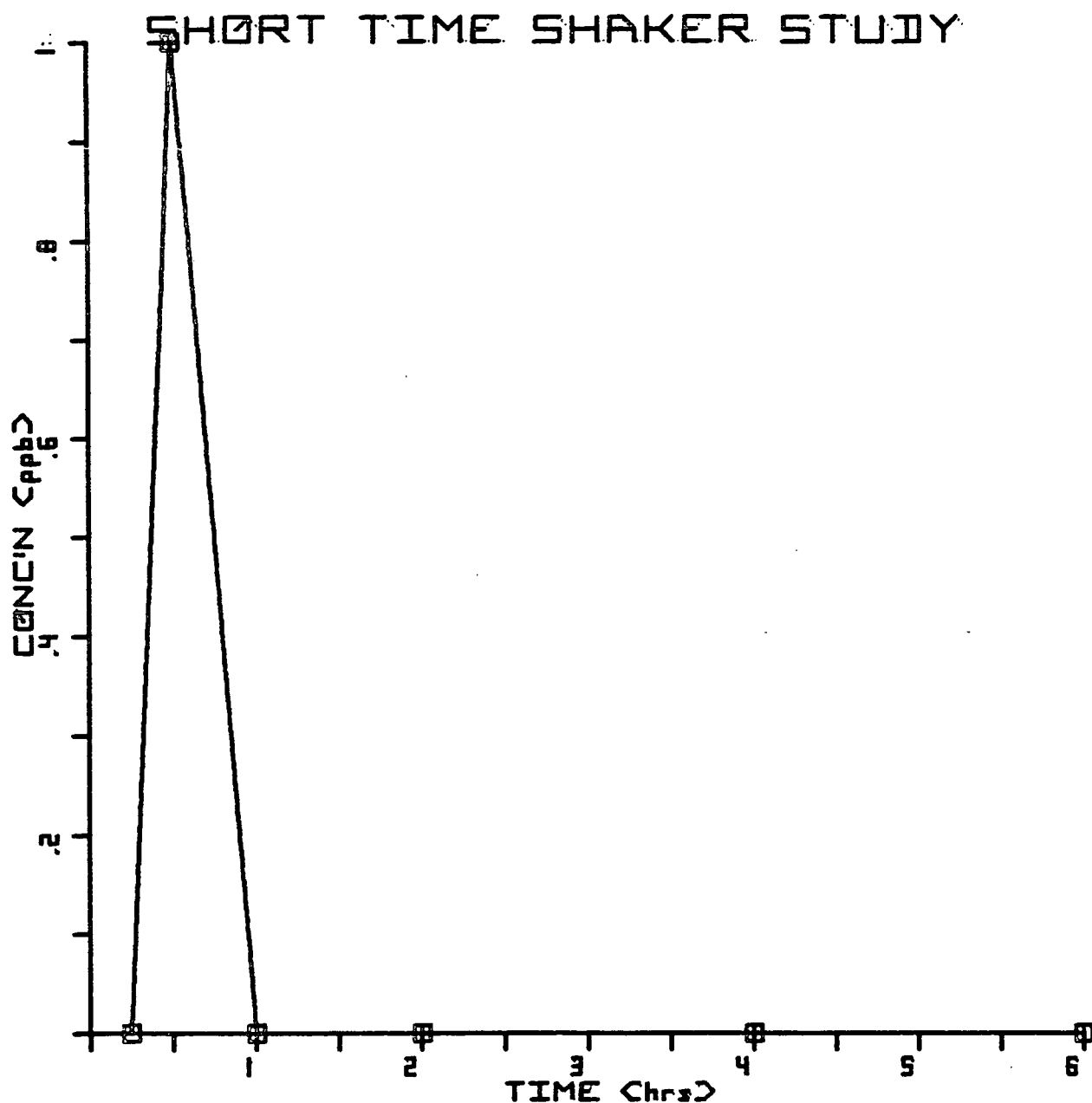                 AIR ATMOSPHERE
                 TOTAL RELEASE

159

SHORT TIME SHAKER STUDY
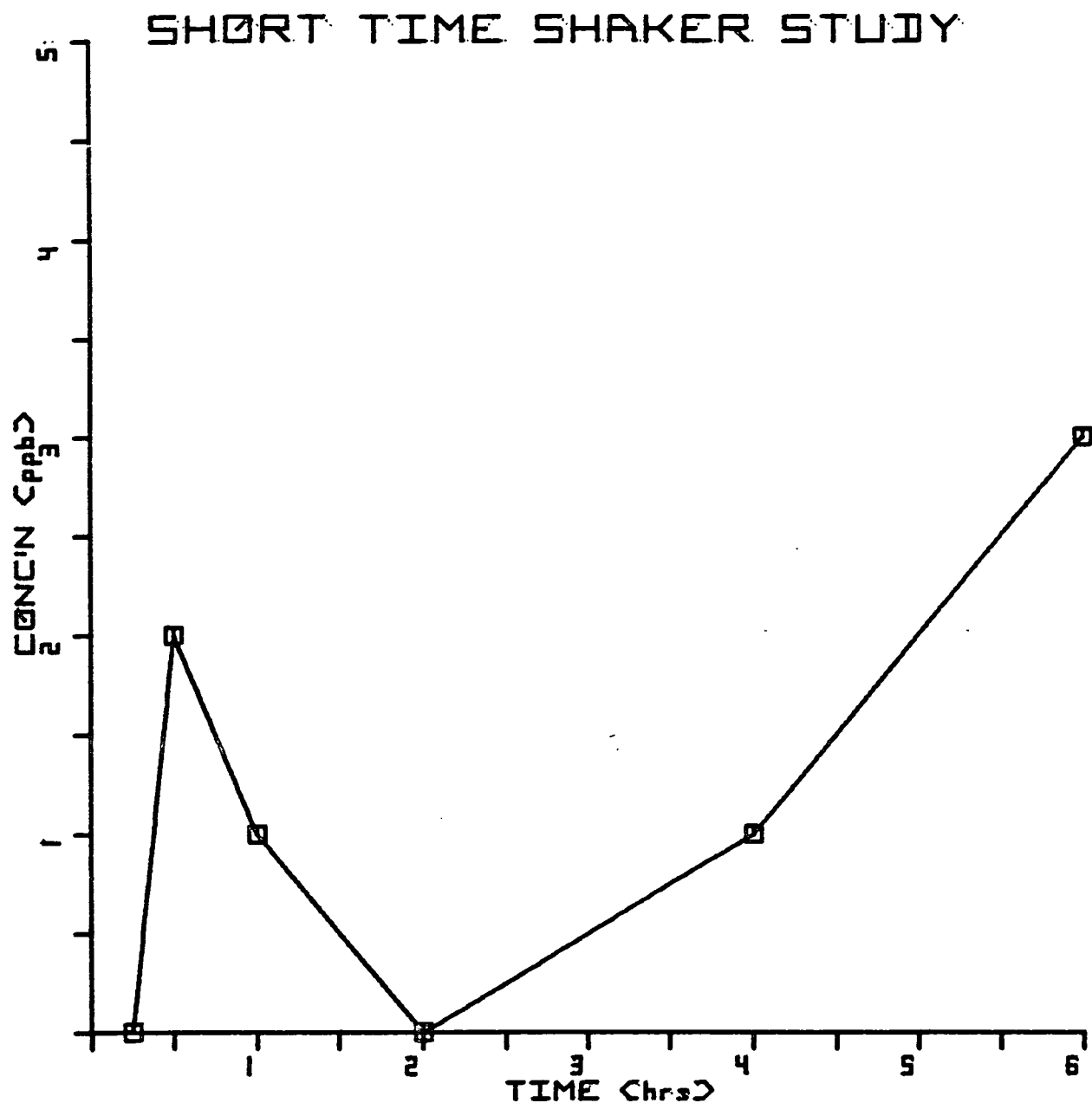
FIGURE V-D-58:     SELENIUM
WESTERN COAL NO. 2 (0.50-1.00 MM)
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO : 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE
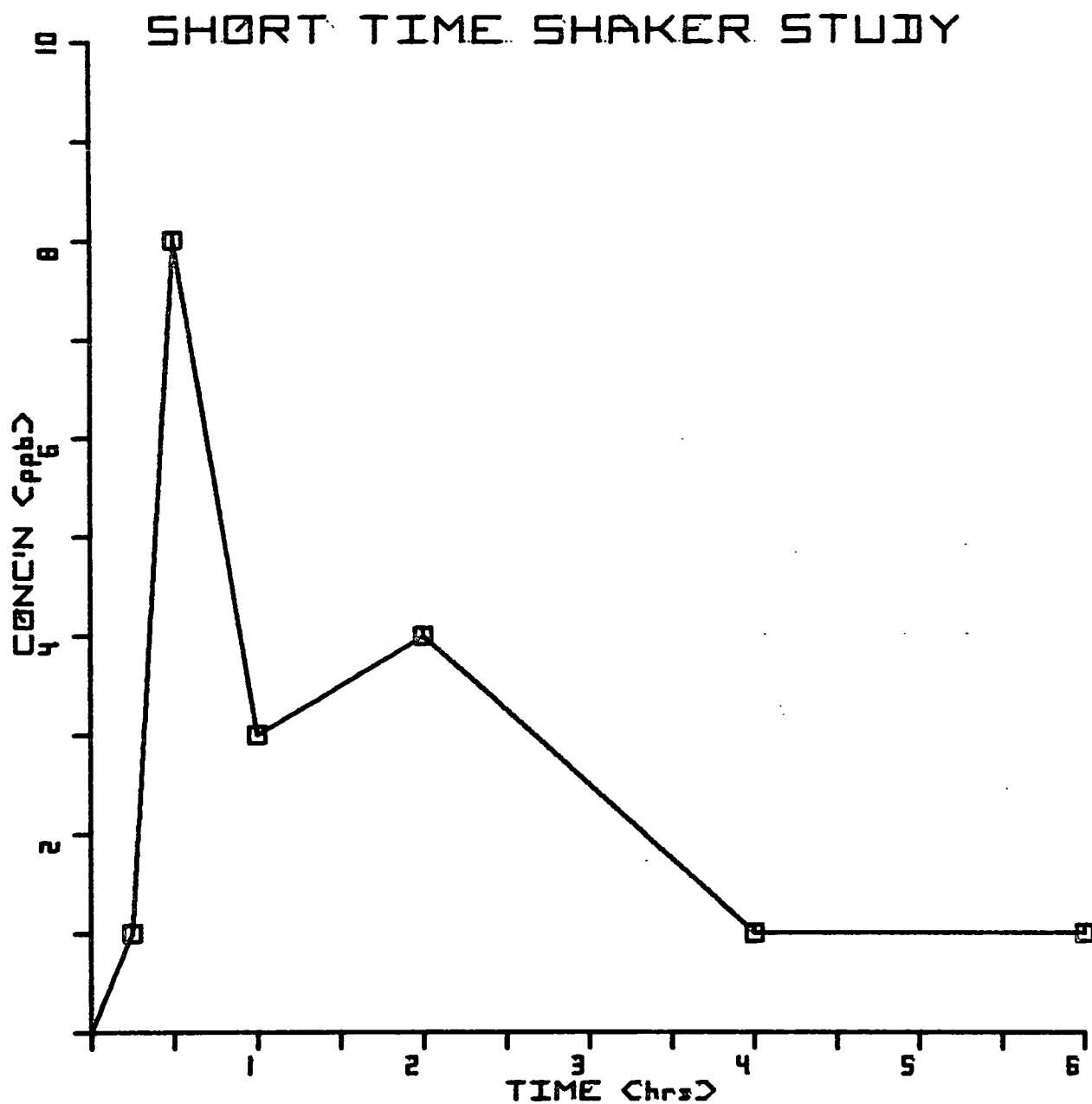
160

# SHORT TIME SHAKER STUDY



FIGURE V-D-59:    ZINC
WESTERN COAL NO. 2 (0.50-1.00 MM)
DEIONIZED WATER LEACHANT
COAL/LEACHANT RATIO : 0.2 G./1.0 G
AIR ATMOSPHERE
TOTAL RELEASE

161

# VI.  ERROR STATISTICS OF ANALYTICAL DATA

Aside from the pooled higher order interactions which were used in the analysis of variance work, some independent statistical measures of precision were needed.  These statistics were calculated from three sources:

1.  Duplicate atomic absorption runs were made on some of the analate solutions.  These measurements, especially ones made at low metal ion concentrations, furnish excellent data for an estimation of detection limits.

2.  A few analate solutions were run repeatedly in the atomic absorption spectrophotometer as a measure of relative instrumental error.

3.  Certain entire runs were duplicated.  These data were analyzed for an estimate of run to run variance.

1.  The Duplicate Atomic Absorption Runs:

The calculated statistics for the low level duplicates are tabulated in Table VI-1 where:

     s    =   the pooled standard deviation in ppb
  d.f.   =   the degrees of freedom
     y    =   average ppb of metal to give 0.001 absorbance unit on the A.A.
               (y is listed for both unpyrolized and pyrolized furnace tubes)
  s/y  =   the calculated ratio of s to y

The blanks in the table are explained as follows:  (a) Cd was always run by standard addition so that no direct y was available, (b) Se was not analyzed in unpyrolized cells and (c) no V was found in any of the samples in this series.

The average of the s/y values from Table VI-1 is 1.57 which gives an average s of 1.57 y.  Then $\sigma \cong 1.57$ y.  Assuming an $\propto$ probability of 0.05 gives 95% confidence limits of $1.96\sigma = 3.08$ y so that an $\propto = 0.05$ detection limit would be about 3 x (concentration to give 0.001 A unit).

This overall estimate compares favorably with the 4 x (concentration to give 0.001 A unit) which has been used as a detection limit estimate (Ref. 1, 1973, unrevised).

These detection limit estimates are used as a basis for rejection of the data for certain metals in certain experiments where the level is too low to warrant further analysis.

162

2.  The standard deviations at very low (near detection limit) measurements
    are not equal to the error expected at larger metal ion concentrations.

This type of error was briefly checked for three metals at medium concentrations.  The results are shown in Table VI-3 and show relative measurement-to-measurement standard deviations in the 3% to 18% range with an average of 11%.  This agrees with the rule of thumb that atomic absorption measurements are precise to within about 10%.

There are, of course, extensive variations in precision depending on metal, metal concentration, age of furnace tube, dilution technique, etc. However, such an investigation is not needed here.  In general, the effects observed are either well above 10% or are based on a sufficient number of observations to reduce the error to tolerable limits.

3.  Run-to-run variances were estimated from the continuous flow, releaching
    study.

These relative standard deviations between runs at each particular time were calculated using:

$$s \text{ relative} = \frac{s}{\bar{x}} = \left( \frac{|X_2 - X_1|}{\sqrt{2}} \right) \cdot \frac{2}{X_2 + X_1} = \sqrt{2} \left| \frac{X_2 - X_1}{X_2 + X_1} \right|$$

The s relative values for each metal and condition were then averaged over the four sampling times using:

$$s_{\text{relative, average}} = \left( \sum_i (s_i)^2 \right)^{1/2}$$

The results are tabulated in Table VI-4.

Evaluating those runs which are at or near detection limits yields a pooled $s_{\text{relative}}$ overall metals and conditions of 18.9%.

The statistical calculations are for the most part, a posteriori to the experiments and do not represent the best estimators that could be designed. Nevertheless, it is felt that values of $s_{\text{relative}} \cong 10\%$ for A.A. analyses and $s_{\text{relative}} \cong 20\%$ for overall run to run results are reasonable estimates of experimental precision when the data is well above detection limits.

TABLE VI-1

Statistics for Low Level Duplicate Runs

| Metal | s | d.f. (for s) | Unpyrolized | Pyrolized | Weighted Average | s/y |
|-------|---|--------------|-------------|-----------|------------------|-----|
| As | 0.319 | 23 | 0.173 | 0.20 | 0.186 | 1.72 |
| Ba | 1.45 | 7 | 4.45 | 2.21 | 3.45 | 0.42 |
| Cd | 0.0267 | 7 | -- | -- | -- | -- |
| Cr | 0.0866 | 18 | 0.172 | 0.072 | 0.122 | 0.71 |
| Co | 0.463 | 7 | 0.34 | 0.108 | 0.166 | 2.79 |
| Cu | 0.253 | 24 | 0.152 | 0.096 | 0.124 | 2.04 |
| Pb | 0.248 | 15 | 0.155 | 0.045 | 0.073 | 3.40 |
| Mn | 0.0809 | 13 | 0.078 | 0.072 | 0.075 | 1.08 |
| Mo | 0.346 | 6 | 2.19 | 0.553 | 0.961 | 0.36 |
| Ni | 0.805 | 9 | 1.36 | 0.252 | 0.569 | 1.41 |
| Se | 0.339 | 7 | -- | 0.31 | 0.31 | 1.09 |
| Zn | 0.127 | 8. | 0.06 | 0.053 | 0.056 | 2.27 |
| V | -- | -- | 7.85 | 3.02 | 4.23 | -- |

TABLE VI-2

Calculated 95% ($\alpha = 0.05$) Detection Limits for Analysis at Low Concentrations

| Metal | 95% Detection Limits (ppb) | |
| --- | --- | --- |
| | Unpyrolized | Pyrolized |
| As | 0.52 | 0.60 |
| Ba | 13 | 6.6 |
| Cr | 0.52 | 0.22 |
| Co | 1.0 | 0.32 |
| Cu | 0.46 | 0.29 |
| Pb | 0.47 | 0.14 |
| Mn | 0.23 | 0.22 |
| Mo | 6.6 | 1.7 |
| Ni | 4.1 | 0.76 |
| Se | --- | 0.93 |
| V | 24 | 9.1 |
| Zn | 0.18 | 0.16 |

Overall estimate for Cd = 0.080 ppb

## TABLE VI-3

### Relative Analytical Errors at Moderate Concentrations

| Metal | Number of Measurements | $\bar{x}$ | s | Relative Error $s/\bar{x}$ % |
|-------|------------------------|-----------|-------|------------------------------|
| Pb    | 9                      | 3.71      | 0.33  | 9.0                          |
|       | 8                      |           |       |                              |
| Ba    | 8                      | 178       | 27.3  | 15.4                         |
|       | 8                      | 135       | 24.3  | 18.0                         |
| Mn    | 8                      | 9.60      | 0.293 | 3.0                          |
|       | 8                      | 18.0      | 0.667 | 3.7                          |

TABLE VI-4

Run to Run Relative Standard Deviations For

Continuous Flow Releaching Studies

| | Mean $s_{relative}$ in % | |
| Metal | Millipore Water Runs (%) | Acetate Buffer Runs (%) |
|---|---|---|
| As | 5.10 | 1.53 |
| Ba | 6.63 | 4.88 |
| Cd | 16.5 | 11.5 |
| Cr | 32.0* | 14.6 |
| Co | 0.0* | 5.63 |
| Cu | 7.03 | 42.4 |
| Mn | 29.3 | 7.29 |
| Mo | 15.4 | 2.81 |
| Se | 27.9 | 49.7* |
| Zn | 34.8 | 15.4 |

Pb, Ni and V were below detection limits, Hg was not analyzed.

*Raw data for these values are at or very near detection limit.

# VII. CHEMISTRY REFERENCES

1. Analytical Methods for Atomic Absorption Spectrophotometry. Perkin-Elmer Technical Manual 303-0152, March 1973, Revised March 1977.

2. Analytical Methods for Atomic Absorption Spectrophotometry Using the HGA Graphite Furnace. Perkin-Elmer Technical Manual 990-9972, 1974.

3. Babu, S. P. 1975. Trace Elements in Fuel. Advances in Chemistry Series 141, American Chemical Society, Washington, D.C.

4. Bilenchi, T. H., H. R. Yates and R. J. Sinnott. 1975. Experience with Decker Coal at Detroit Edison's St. Clair Power Plant. Proceedings of the American Power Conference, Vol. 37.

5. Capes, McIlhinney, Russell and Serianic. 1974. Rejection of Trace Metals from Coal During Beneficiation by Agglomeration. Env. Sci. and Technology 8, 35-38.

6. Chadwick, R. A., R. A. Woodruff, R. W. Stone and C. M. Bennett. 1975. Lateral and Vertical Variations in Sulfur and Trace Elements in Coal-- Colstrip Field, Montana. Proceedings of the Fort Union Coal Field Symposium, Vol. 3, Montana Academy of Sciences, Eastern Montana College, Billings, Montana, April 25-26.

7. Davies, O. L. 1963. The Design and Analysis of Industrial Experiments. Hafner Publishing Company, New York.

8. Environmental Impact Report, Coal Transshipment Facility, Superior, Wisconsin. 1974. Prepared by Roy F. Weston, Inc., Wilmette, Illinois, July.

9. Glass, G. E. and J. E. Poldoski. 1974. Interstitial Water Components and Exchange Across the Water Sediment Interface of Western Lake Superior. XIX Congress, International Association of Limnology (SIL) Winnipeg, Canada, April 22-29.

10. Manning, D. C. 1970. Non-Flame Methods for Mercury Determination by Atomic Absorption--A Review. Atomic Absorption Newsletter 9, 97.

11. Manual of Methods for Chemical Analysis of Water and Wastes. 1974. Methods Development and Quality Assurance Laboratory, U.S. Environmental Protection Agency, Publication EPA-625-6-74-003.

12. Paus, P. E. 1972. Bomb Decomposition of Biological Materials. Atomic Absorption Newsletter 11, 129.

13. Poldoski, J. E. and G. E. Glass. 1974. Methodological Considerations in Western Lake Superior Water-Sediment Exchange Studies of Some Trace Elements. Presented at the 7th Materials Symposium, National Bureau of Standards, Gaithersburg, Maryland, October 7-11.

14. Report to the International Joint Commission by the Upper Lakes Reference Group. 1976. The Waters of Lake Huron and Lake Superior. Vol. 1, Windsor, Ontario.

15. Smeyers-Verbeke, Michotte, Van den Winkel and Massart. 1976. Matrix Effects in the Determination of Copper and Manganese in Biological Materials Using Carbon Furnace Atomic Absorption. Anal. Chem. 48, 125.

16. Sturgeon, R. E. and C. L. Chakrabarti. 1977. Evaluation of Pyrolytic-Graphite-Coated Tubes for Graphite Furnace Atomic Absorption Spectrophotometry. Anal. Chem. 49, 90.