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Oxidation of molybdenite with the aid of microorganisms

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OXIDATION OF MOLYBDENITE WITH THE AID OF MICROORGANISMS

A THESIS

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DEDICATION

This work is dedicated to my wife Beverley and daughter Lynette.

This Thesis by Ralph Anderson is accepted in its present form by the Department of Chemistry and Chemical Engineering as satisfying the Thesis requirement for the degree of Master of Science.

Signed,

ACKNOWLEDGMENTS

The author wishes to extend thanks to Dr. Loren C. Bryner for his assistance in the planning and execution of this investigation. The author also wishes to express his gratitude for the many helpful comments and suggestions from the faculty of the Chemistry Department and fellow students.

The author desires to acknowledge the aid of the Utah Copper Division of the Kennecott Copper Corporation for supporting this work.

To my wife, Beverley, I extend my sincere appreciation for whose patience and inspiration contributed extensively to the completion of this work.

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CHAPTER I

INTRODUCTION

Molybdenum occurs in group VIB of the periodic table. The elements in this group are characterized by high melting points, toughness, and a maximum valence of six. In the hexavalent state these metals have many properties in common and show a pronounced tendency to form poly-acids.[1]

Molybdenum is a hard, silver-white metal long recognized as a substance with distinctive properties. It has an atomic weight of 95.95, an atomic number of 42, a specific gravity of 10.2, a melting point of 2626°C., and a boiling point of 3700°C. Molybdenum has the oxidation states of plus 2, 3, 4, 5, and 6.[2] It has assumed commercial importance within comparatively recent time.[3]

Although a dozen or more minerals contain molybdenum, molybdenite is the principal one. Table I gives some of the more common molybdenum minerals.[4,5]

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[1]A. Linz, "Molybdenum Chemistry," Ind. Eng. Chem., Vol. 47 (Aug. 1955), pp. 1492-1493.

[2]P. R. Frey, College Chemistry, Prentice-Hall, Inc., New York, 1952, p. 540.

[3]B. H. Danziger and C. H. Kline, "Molybdenum Chemicals," Chem. Eng. News, Vol. 33, No. 3 (Jan. 17, 1955), pp. 268-272.

[4]L. T. Fairhall, R. C. Dunn, N. E. Sharpless, and E. A. Pritchard, "The Toxicity of Molybdenum," U. S. Print. Office, 1945, pp. 5-7.

[5]W. Van Royen and O. Bowles, The Mineral Resources of the World, Prentice-Hall, Inc., New York, 1952, p. 84.

TABLE I

PRINCIPAL MOLYBDENUM CONTAINING ORES[4,5]

Name	Formula	Per Cent Molybdenum
Molybdenite	MoS_2	59.70
Wulfenite	$PbMoO_4$	26.14
Powellite	$Ca(Mo,W)O_4$	25.0
Molybdenum Ocre	$FeMoO_4$	44.50

Molybdenite, MoS_2, occurs as black, shiny-blue, or dark gray hexagonal plates as sheets usually closely mixed with quartz or other siliceous material.[4] Up to the middle of the eighteenth century the mineral molybdenite was supposed to be identical with graphite, then known as "plumbago" or "black lead." In 1778 K. W. Scheele in his Treatise on Molybdena showed that, unlike plumbago or graphite, molybdenite forms a "perculiar white earth" when treated with nitric acid. This he proved to have acid properties and he called it "acid molybdenae," that is, molybdic acid; and he correctly considered the mineral molybdenite to be a molybdenum sulfide. In 1790 P. J. Hjelm isolated the element as a metallic powder by heating molybdic acid with charcoal.[6]

The crude ore is seldom higher than five to six per cent MoS_2 and material containing as little as one-half per cent MoS_2 can be concentrated efficiently. This sulfide has a soft, greasy texture and is difficult to distinguish by appearance from graphite.[4]

The molybdenite ore, after a certain amount of hand picking, is pulverized and concentrated by oil floatation. Figure 1 shows the

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[6] G. D. Parkes, Mellor's Modern Inorganic Chemistry, Longmans, Green and Co., New York, 1952, p. 816.

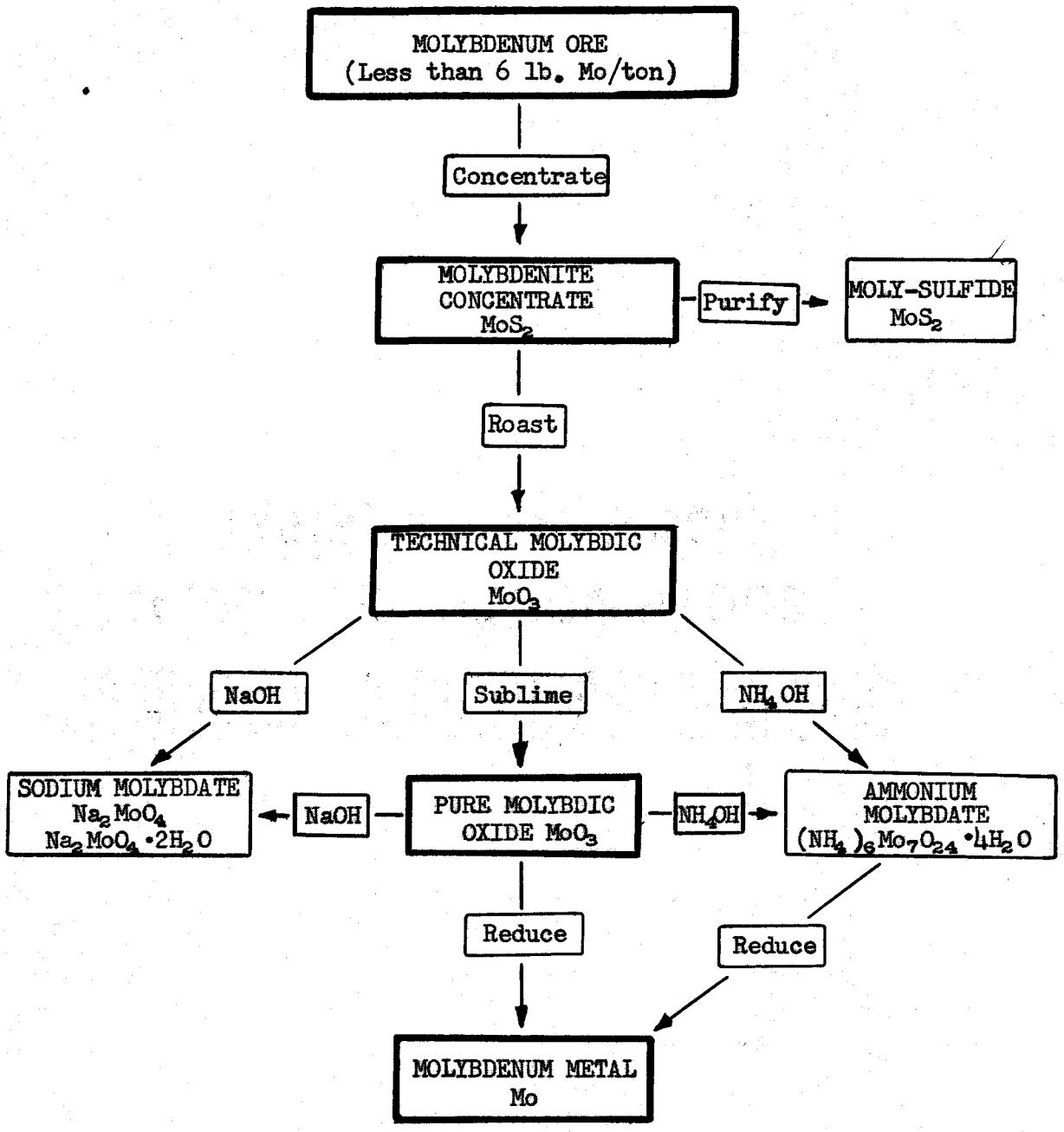

Fig. 1 Process steps in producing bulk molybdenum products.[1]

different steps in the refinement of molybdenite ore and the production of molybdenum metal along with a few derivatives.[1]

The molybdenum resources of the United States comprise a larger portion of known world resources than those of any other metal in common use.[5] The reserves of molybdenum in the United States were reported in 1947 as 2,600,000,000 pounds of metal in ores considered commercial in current practice, 900,000,000 pounds in potentially commercial and marginal ores, and 3,500,000,000 in submarginal ores. There are known reserves for one hundred years at the highest recorded rate of consumption.[7]

The principal sources in the United States are: (1) those that yield molybdenum as the sole or dominant product, represented by the deposits at Climax, Colorado; Questa, New Mexico; and Urad (Empire), Colorado; and a number of smaller deposits that are worked on sporadically; and (2) certain disseminated copper deposits that yield molybdenite after treatment of the copper concentrates.

The worlds largest reserves of molybdenum ore are in the famous deposit at Climax, Colorado. This deposit is a huge mass of finely brecciated granite carrying tiny veinlets filled with quartz and molybdenite. For twenty-three consecutive years it was the top producer until 1947 when the Utah Copper Division of the Kennecott Copper Corporation, which recovers molybdenite as a by-product from its copper concentrates, became the major producer of the metal.[5]

Figure 2 shows an estimated production comparison of molybdenum and molybdenum compounds both in the United States and the world for the years of 1935 to 1953.[2]

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[7]Clifford A. Hampel, Rare Metals Handbook, Reinhold Publishing Corporation, New York, 1954, p. 272.

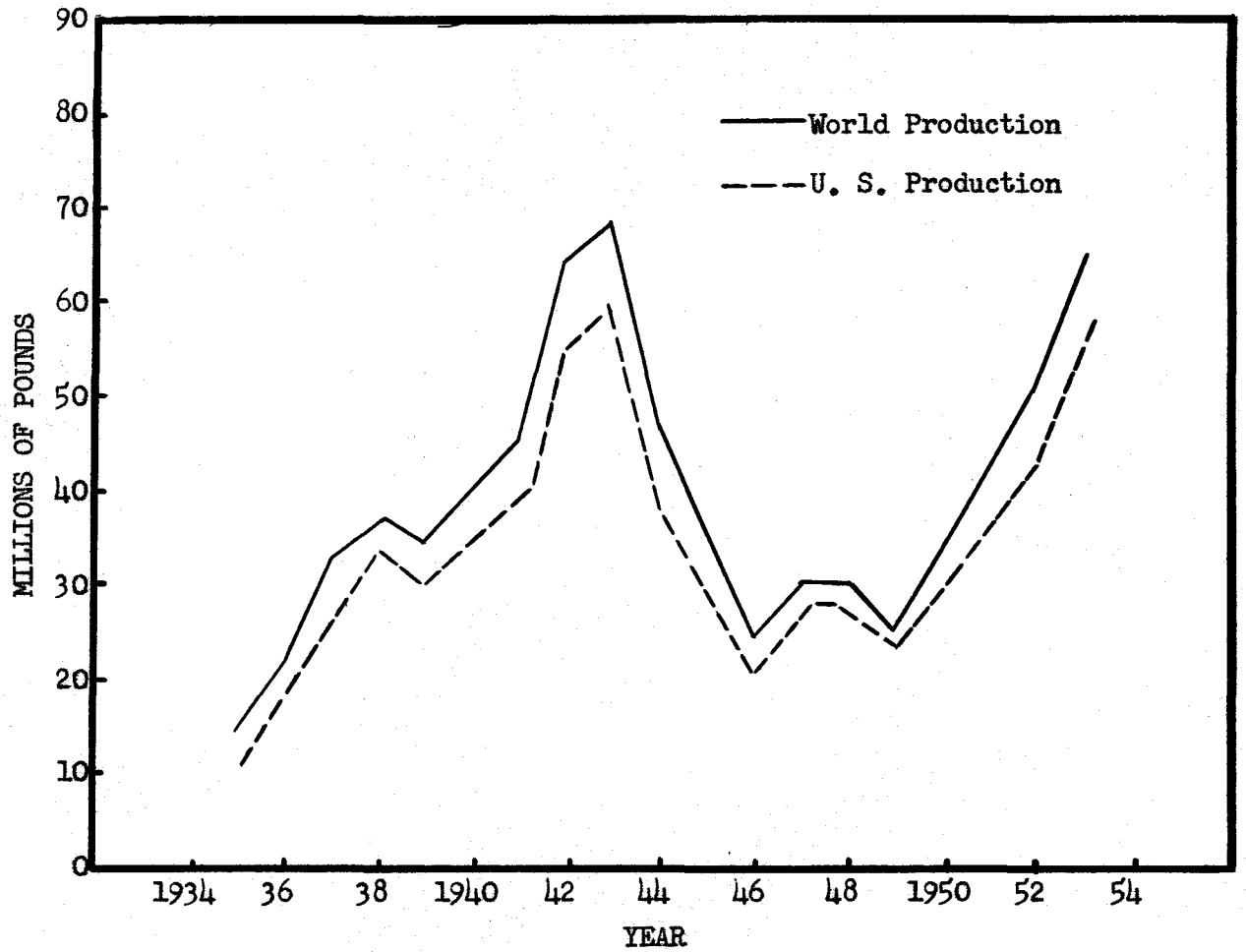

Fig. 2 Production of molybdenum (as metal contained in mine concentrates).[2]

Molybdenum is a transition element with an electronic structure favorable to catalytic activity. In 1955 it was estimated that nearly 1,200,000 pounds of molybdenum were consumed in the manufacture of catalysts.[2] A recent digest of the literature through 1947[8] summarizes some 535 articles and 1755 patents on molybdenum catlysts.

Because of the similarity of molybdenite to graphite it has attained possibly its greatest industrial use as solid lubricants for high temperatures and pressures. Studies have shown that the coefficient of kinetic friction is less for molybdenite than for graphite[9] and that molybdenite is quite stable at relatively high temperatures.[10]

Molybdenum and a number of its derivatives have assumed economical importance in inorganic pigments,[11] organic pigments,[12] plant requirements,[13] and quantitative analyses.[14]

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[8]J. Lavollay, Compt. rend. acad. agr. Vol. 28, 1942, pp. 353-354.

[9]R. L. Johnson, D. Godfrey, and E. E. Bisson, "Friction of Solid Films on Steel at High Sliding Velocities," National Advisory Committee for Aeronautics, Washington D. C., April 1948.

[10]D. Godfrey and E. C. Nelson, "Oxidation Characteristics of Molybdenum Disulfide and Effect of Such Oxidation in its Role as a Solid Film Lubricant," National Advisory Committee for Aeronautics, Washington D. C., May 1949.

[11]W. G. Huckle and E. Lalor, "Inorganic Pigments," Ind. Eng. Chem., Vol. 47, (Aug. 1955) pp. 1507-1510.

[12]W. W. Williams and J. W. Conley, "Organic Pigments," Ind. Eng. Chem., Vol. 47 (Aug. 1955), pp. 1507-1510.

[13]C. J. Rodden, Analytical Chemistry of the Manhattan Project, Vol. 1, McGraw-Hill Book Co., Inc., 1950.

CHAPTER II

BASIS OF THE PROBLEM

It has been assumed until recently that molecular oxygen from the air was responsible for the oxidation of pyrites and chalcopyrites. This would account for the presence of soluble iron and copper in the acid mine waters and for the weathering of sulfide minerals that are located on the surface of the earth's crust.

Investigators working with pyrite ores have reported that the oxidation is very small under controlled conditions. Studies[1,2] in this laboratory have shown that less than two-tenths of one per cent of the pyrite sample underwent oxidation. Carmichel[3] supports these findings on pyrite and in addition reports that after thirteen days of continuous agitation in the presence of water and oxygen, only two-hundreths of one per cent of chalcopyrite underwent oxidation.

The presence of iron and sulfuric acid in the drainage water from coal mines in the bituminous areas of Pennsylvania and West Virginia has been studied by Leathen[4] and others. Their results indicate that the

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[1]W. O. Ursenback, "Factors Influencing the Moist Oxidation of Iron Pyrites," (Unpublished Master's Thesis, Department of Chemistry, Brigham Young University, 1948).

[2]N. L. Jensen, "Factors Influencing the Solubility and Oxidation of Commercial Iron Pyrites," (Unpublished Master's Thesis, Department of Chemistry, Brigham Young University, 1949).

[3]T. Carmichel, University of Toronto Studies, Geological Services, 1926.

[4]W. W. Leathen, S. A. Braley, and L. D. McIntyre, Applied Microbiology, I, 1953, pp. 61-68.

iron and acid in coal mine waters were due to the oxidation of exposed sulfuritic materials in the mine deposits. Beckwith[5] has reported the action of certain Thiobacillii on iron sulfide. The pH studies in his work show the possibility of oxidative action on pyrites: chalcopyrite ($CuFeS_2$), marcasite (FeS_2), and pyrrhotite (Fe_5S_6-$Fe_{16}S_{17}$) by soil microorganisms.

Wilson[6,7] and Davis[7,8] in this laboratory have shown that the microorganisms found in the mine waters of Bingham Canyon were able to oxidize iron pyrite to sulfuric acid, ferrous sulfate, and ferric sulfate and that most of the soluble copper in acid mine leaching was the product of biological oxidation of copper sulfide ores. Soluble copper was readily formed from all the copper-containing sulfides investigated. The minerals studied were Bingham Canyon float concentrate, chalcopyrite ($CuFeS_2$), covellite (CuS), chalcocite (Cu_2S), bornite (Cu_5FeS_4), tetrahedrite ($Cu_8Sb_2S_7$), and reagent grade CuS.

The evidence is quite conclusive that sulfide minerals of iron and copper can be oxidized and leached by the aid of microorganisms. This led to the express purpose of this study to investigate the possibility of the biological oxidation of molybdenite (MoS_2), to determine the physical and chemical conditions under which the oxidative process

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[5]T. D. Beckwith, Gas, Vol. 21, No. 12, 1945, pp. 47-48.

[6]D. C. Wilson, "Studies on the Biological Oxidation of Iron Pyrite," (Unpublished Master's Thesis, Department of Chemistry, Brigham Young University, 1952).

[7]L. C. Bryner, J. V. Beck, D. B. Davis, and D. C. Wilson, Industrial and Engineering Chemistry, Vol. 46, Dec. 1954, p. 2587.

[8]D. B. Davis, "Biological Oxidation of Copper Sulfide Minerals," (Unpublished Master's Thesis, Department of Chemistry, Brigham Young University, 1953).

occurs, and to develop a strain of bacteria or alter the activity of the microorganisms by acclimatization to increase their activity on sulfide minerals, in particular molybdenite.

CHAPTER III

EXPERIMENTAL METHODS AND PROCEDURES

A. The Apparatus

The main apparatus and technique used in this study were previously developed in this laboratory.[1] The equipment consisted as shown in Figure 3 of slightly modified air lift percolators in groups of sixteen, making a total of sixty-four divided into four banks. The percolators were constructed from 40 mm pyrex glass tubing approximately 400 mm in length. The mineral samples and the Ottawa sand were supported in the percolator by a perforated porcelain disk, resting in the constricted bottom, covered with approximately fifteen mm of pyrex glass wool. The sand and glass wool were used to retain the finely divided minerals. An exterior 5 mm glass tube was sealed to the base of the percolator and the other end joined to the side of the percolator 200 mm from the top. This tube was attached by the means of a short side arm to a source of compressed air which served as a lifting device and the source of carbon dioxide and oxygen. The percolator was drained through an opening in the bottom which was attached to a short piece of rubber tubing closed with a pinch clamp. A cotton plug was placed in the top of the percolator to keep out dust, prevent contamination, and permit the air to escape. The air was saturated by bubbling it through an aerator containing distilled water to reduce evaporation from the leaching

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[1] L. C. Bryner, J. V. Beck, D. B. Davis, and D. C. Wilson, Industrial and Engineering Chemistry, Vol. 46, Dec. 1954, p. 2587.

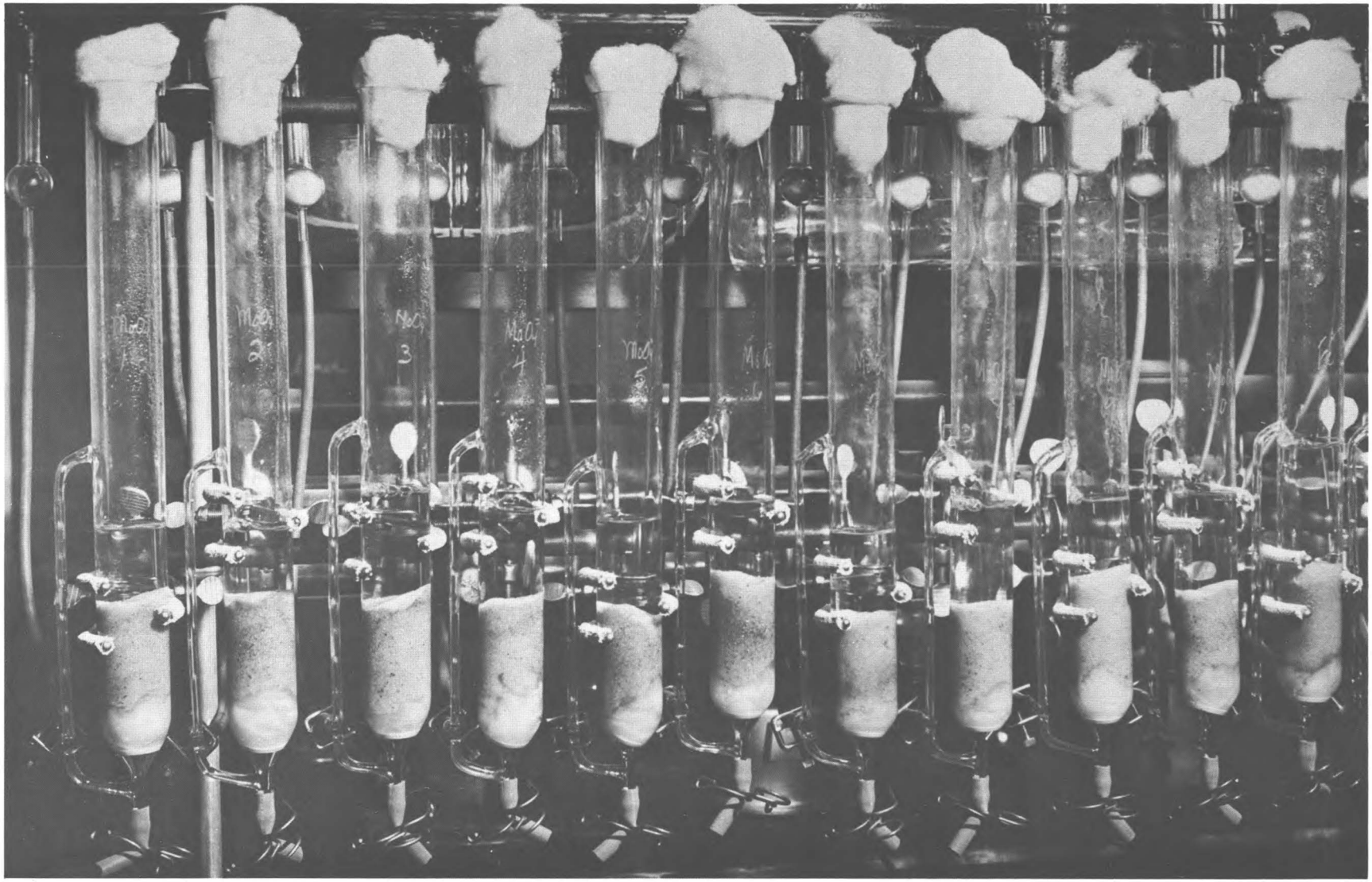

Fig. 3 A series of percolators used in the investigation.

solution. The air was filtered through a cotton plug in the delivery tube to prevent contamination and remove foreign material. The delivery tube was attached to the percolator and the rate of air flow was regulated by a screw clamp on the delivery tube to permit approximately one bubble per second in the lifting channel. The air supply was regulated by a reduction valve and once adjusted needed very little attention.

The charge of a percolator consisted of 100 grams of Ottawa sand (SiO_2) and 5 grams of the desired mineral thoroughly mixed by agitation in a container. A special funnel was used as a charging tube to keep the minerals which tend to settle dispersed as evenly as possible. This funnel was placed in the percolator resting on the pyrex glass wool and then filled with the charge by washing the mineral and sand mixture into the funnel with water. The charging funnel was then lifted slowly to allow the contents to settle evenly in the percolator over the glass wool.

One hundred ml of nutrient solution was added to the charged percolator and the percolator was attached to the support rack. The air inlet was then connected to the air source. The percolators that were run as sterile controls were sterilized in an autoclave and from this point on precaution was taken to avoid contamination. After allowing the percolators to run for one week, they were drained and refilled with sterile nutrient. At this point the percolators were inoculated with the desired culture except those that were to be used as controls.

At the end of every seven days the percolators were drained and analyzed for the desired soluble components. The percolators were refilled immediately with 100 ml of fresh nutrient solution.

The results of the investigations are recorded in tables and represented in graphical form.

B. The Sulfide Minerals

The samples of iron pyrite Nos. I and II, molybdenite concentrate, molybdenite ore No. I, and chalcopyrite were obtained from the Utah Division of Kennecott Copper Corporation. The samples of pyrite Nos. III, IV, and V were obtained from the Brigham Young University Geology Department.

The sulfide minerals were ground if necessary so that approximately sixty per cent passed a two hundred mesh screen. The mineral samples recovered by flotation were washed with acetone and distilled water to remove any foreign material that might be toxic to the microorganisms used in this investigation. The analyses of the sulfide minerals are given in Table II.

TABLE II

ANALYSES OF THE SULFIDE MINERALS

Sulfide Mineral	% Mo	% S	% Cu	% Fe	% Insol.
Molybdenite Concentrate	57.58	38.42	0.1	0	3.9
Molybdenite Ore	0.871	0.903	0.271	0.756	97.199
Pyrite No. I	trace	49.9	0.95	42.25	6.8
Pyrite No. II	trace	46.4	1.8	41.1	8.4
Pyrite No. III	0.04	44.45	6.57	46.0	0.08
Pyrite No. IV	trace	48.3	5.04	44.2	2.46
Pyrite No. V	trace	42.5	5.36	34.25	17.89
Chalcopyrite No. II	trace	33.45	32.15	18.55	15.85

C. The Microorganisms and Nutrient Requirements

The microorganisms used in this study were obtained from the

leaching streams in Bingham Canyon, Utah. They were the same type used in this laboratory on the biological oxidation of pyrite[1,2] and copper sulfide minerals.[1,3]

These bacteria are autotrophs which require carbon dioxide and oxygen from the air along with other inorganic substances, in this case iron pyrite, molybdenite, or other sulfide minerals. The oxidation of the minerals is the source of the energy for the bacteria. Their needs for carbon dioxide and oxygen are satisfied by the air supplied to the percolators. The importance of carbon dioxide has been previously shown on the biological oxidation of pyrite.[2] The bacteria are short rods similar to thiobacillus thio-oxidans[4] or thiobacillus ferro-oxidans.[5]

TABLE III

THE BACTERIAL CULTURES

Culture	Source
I	Bingham Canyon leaching streams
II	Molybdenite concentrate medium
III	Molybdenite concentrate and pyrite medium
IV	Molybdenite concentrate and chalcopyrite medium

[2]D. C. Wilson, "Studies on the Biological Oxidation of Iron Pyrite," (Unpublished Master's Thesis, Department of Chemistry, Brigham Young University, 1952).

[3]D. B. Davis, "Biological Oxidation of Copper Sulfide Minerals," (Unpublished Master's Thesis, Department of Chemistry, Brigham Young University, 1953).

[4]S. A. Waksmans, "Thio Oxidans," J. of Bact., 7, 239, (1922).

[5]Temple and Colmer, "The Autotrophic Oxidation of Iron by a New Bacterium: Thiobacillus Ferro-oxidans," J. of Bact., 62, 605 (1951).

There were many transfers of the bacteria throughout this investigation. Table III shows the culture and source of the microorganisms.

The nutrient requirement for the autotrophic bacteria was developed in this laboratory on the biological oxidation studies of pyrite and copper sulfide minerals. The composition of this nutrient (No. I) medium is given in Table IV.

TABLE IV

NUTRIENT NO. I[1,2,3]

Component	Weight in Grams
Ammonium sulfate, $(NH_4)_2SO_4$	1.0
Potassium hydrogen phosphate, K_2HPO_4	0.3
Aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$	8.0
Magnesium sulfate, $MgSO_4 \cdot 7H_2O$	3.0
Calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$	0.1
Manganese sulfate, $MnSO_4 \cdot H_2O$	0.05
Sodium sulfate, Na_2SO_4	0.05
Potassium chloride, KCl	0.05
Distilled water	1000
pH adjusted to 2.65 with H_2SO_4	

When it was found that these microorganisms successfully oxidized molybdenite, more studies were performed to determine the optimum concentrations of some of the inorganic components in the basic medium. This resulted in an alteration of two components in nutrient No. I, and a second improved nutrient No. II was used. The composition of nutrient No. II is given in Table V.

TABLE V

NUTRIENT NO. II

Component	Weight in Grams
Ammonium sulfate, $(NH_4)_2SO_4$	1.0
Potassium hydrogen phosphate, K_2HPO_4	0.1
Aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$	4.0
Magnesium sulfate, $MgSO_4 \cdot 7H_2O$	3.0
Calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$	0.1
Manganese sulfate, $MnSO_4 \cdot H_2O$	0.05
Sodium sulfate, Na_2SO_4	0.05
Potassium chloride, KCl	0.05
Distilled water	1000
pH adjusted to 2.65 with H_2SO_4	

D. Methods of Analyses

The extent of the biological oxidation of the sulfide minerals was determined by the analysis of the soluble components found in the leaching solution. The products found in solution, depending upon the mineral being used, were ferrous and ferric iron, copper, pentavalent (Mo_2O_5) and hexavalent (MoO_3) molybdenum, and sulfuric acid. The acidity was followed by pH measurements.

1. Determination of Molybdenum

The first attempt to analyze for molybdenum employed a Beckman Model D.U. Flame Spectrophotometer.[6] A wave length of 540 millimicrons was selected to obtain the greatest intensity on the flame to insure

[6]H. H. Willard, L. L. Merritt, Jr., and J. A. Dean, Instrumental Methods of Analysis, D. Van Nostrand Company, Inc., New York, 1951, p. 77.

accuracy. This was a rapid and simple analysis but proved undesirable because of the interference of high concentrations of copper and iron. The results shown in Figure 4 point out the very small intensity of molybdenum compared with the intensity of iron and copper. This indicates that a small error in the copper or iron determination would result in a large error in the molybdenum analysis. After comparing results, the flame spectrophotometer method was discontinued.

The molybdenum was determined by two methods[7,8] which employ the thiocyanate-stannous-chloride colored complex formed with the pentavalent state of molybdenum. The first procedure utilized a butyl acetate extraction of the thiocyanate molybdenum complex while in the second method extraction was not necessary. The extraction method was employed when the copper concentration was greater than twenty parts per million. The cupric ion reacted with the stannous chloride and thiocyanate to give a milky precipitate which interfered in the colorimetric analysis at high concentrations.

In an acid solution, in the presence of a suitable reducing agent such as stannous chloride, the thiocyanate ion gives an amber to orange-red color. The color is due to a thiocyanate complex of pentavalent molybdenum, which can be extracted by organic solvents such as ethyl ether, butyl acetate, or cycohexanol. Babko[9] has pointed out that various complexes can be formed between pentavalent molybdenum and thiocyanate.

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[7]Scott, Standard Methods of Chemical Analysis, Vol. I, D. Van Nostrand and Co., Inc., New York, 1938.

[8]E. B. Sandell, Colorimetric Determination of Metals, Interscience Publishers, Inc., New York, 1950, p. 375.

[9]A. K. Babko, J. Gen. Chem. (U.S.S.R.), 17, 642 (1947): Chem. Abst. 42, 476.

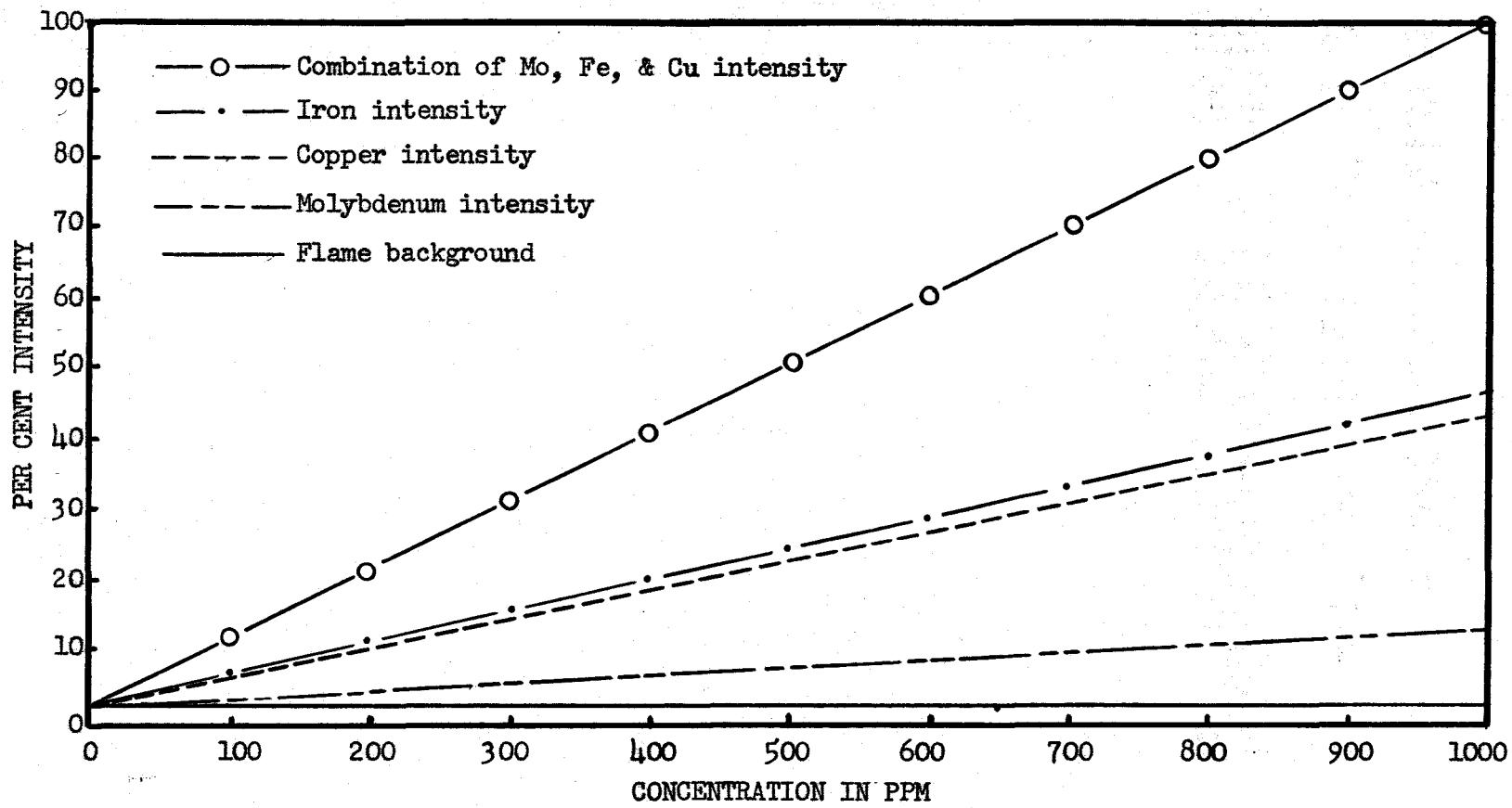

Fig. 4 The flame intensities of Fe, Cu, and Mo vs. their concentrations.

$$Mo^{+5} + mCNS^{-} \rightleftharpoons [Mo(CNS)_m]^{5-m} \quad \text{(Colorless)}$$

$$[Mo(CNS)_m]^{5-m} + (5-m)CNS \rightleftharpoons Mo(CNS)_5 \quad \text{(Red)}$$

The two transitions occur at about 0.005 and 0.08 M thiocyanate concentration respectively. A thiocyanate concentration of 0.2 to 0.4 M results in a weakening of the color.

The color intensity depends upon a number of factors such as the acidity, the thiocyanate ion concentration, and the time of standing.[10] It has been determined that the acidity of the solution in hydrochloric acid should be approximately five per cent and the thiocyanate concentration be 0.6 per cent or greater in the final volume.

The time element in the extraction method was found not to be critical, but in the non-extraction method the color intensity should be measured within five minutes.

The analyses indicated that all of the soluble molybdenum was either in the pentavalent or hexavalent state. This was determined by oxidizing a known amount of the solution from a percolator and also taking the same aliquot of sample without oxidizing it. Table VI compares the quantity of molybdenum determined colorimetrically in the oxidized and nonoxidized form.

From these results given in Table VI one can see that the molybdenum is in the proper oxidized form for analysis.

A wave length vs. absorbancy curve was prepared on a molybdenum thiocyanate solution to determine the proper wave length. This is shown in Figure 5 and a wave length of 525 millimicrons was chosen to obtain the desired range and accuracy.

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[10] L. D. Hurd and H. O. Allen, Ind. Eng. Chem., Anal. Ed., 7, 396 (1935).

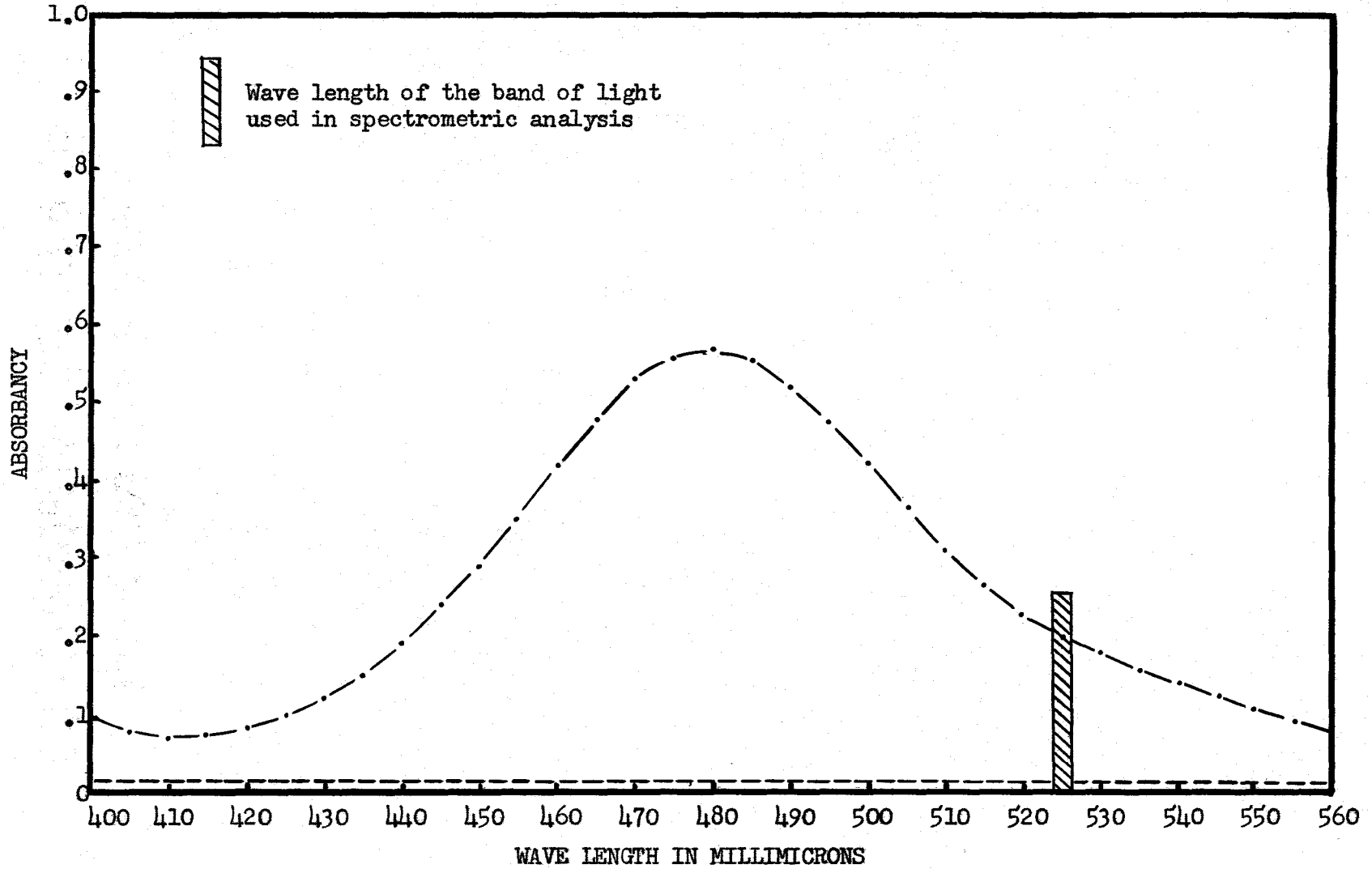

Fig. 5 Absorbance of molybdenum thiocyanate complex vs. wave length.

TABLE VI

COMPARISON OF OXIDIZED TO NONOXIDIZED PERCOLATOR SOLUTION

Oxidized Mo in mg	Nonoxidized Mo in mg
6.2	6.2
3.5	3.49
4.9	4.91
3.0	3.01
8.4	8.39

a. Procedure for Molybdenum Determination Using Butyl Acetate as the Extracting Solvent[7]

The solutions from the percolators were drained into 100 ml volumetric flasks and diluted to exactly 100 ml. After thoroughly shaking the flasks a 2 ml aliquot of sample was placed in a 100 ml separatory funnel along with 3 ml of ten per cent NaCNS solution, 2.0 ml of 12 N HCl, and one ml of ferrous ammonium sulfate solution (unless iron was already present in amount greater than one mg). After vigorously shaking the separatory funnel and contents for ten seconds, 3 ml of ten per cent $SnCl_2$ solution was added (more if much iron was present) and diluted with distilled water to 25 ml and again shaken. Exactly 25 ml of butyl acetate was added and then shaken vigorously for one-half minute. The liquid layers were allowed to separate, the colored butyl acetate layer drawn off, and the absorbancy was determined using reagent butyl acetate as a reference. The results were checked periodically with standards. The analyses were performed on a Coleman Universal Spectrophotometer.

b. Procedure for Molybdenum Determination Without Extraction[8]

Two ml of sample was placed in a 25 ml volumetric flask. Two ml of concentrated HCl, 0.5 ml of one per cent ferrous ammonium sulfate (dissolved in 0.2 N sulfuric acid), 2 ml of ten per cent sodium thiocyanate solution, and 2 ml of ten per cent stannous chloride solution were added and the contents were diluted to 25 ml with distilled water. After allowing sufficient time to establish equilibrium, the absorbancy was determined within five minutes. This procedure was used if the copper concentration was less than 20 ppm.

When the solution could be analyzed in a relatively short time, the reagents were combined before addition to the sample. If the copper was present in the range of 20 to 150 ppm, one ml of Amberlite IR-120 ion exchange resin was added to the 25 ml volumetric flask before addition of the reagents. The resin adsorbed the copper ion avoiding its interference. A standardization curve was made to correct for the resin volume.

2. Determination of Iron

The iron content of the leachates was determined by three methods: a colorimetric method using ortho-phenanthroline[8] for very small amounts, the flame spectrophotometer[6] for medium ranges, and a volumetric method employing potassium dichromate[11] at higher concentrations.

The ortho-phenanthroline method[8] is rapid and sensitive for the determination of iron in very minute quantities and is based on the formation of an orange-red complex, $(C_{12}H_8N_2)_3Fe^{++}$. The color intensity is independent of the acidity in the pH range of two to nine. The complex is very stable and the solutions show no change in color after many

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[11]Pierce and Haenisch, Quantitative Analysis, 3rd Ed., John Wiley and Sons, Inc., New York, 1948, p. 490.

months. Beer's Law is closely followed.

The Beckman Flame Spectrophotometer method[6] provided a very dependable and rapid means of analyzing for iron in solution.

The potassium dichromate method[11] is an accurate and rapid volumetric method. Ferrous iron in solution is titrated with standard potassium dichromate solution. Diphenylamine sulfonic acid[11] indicator gave a very good end point. This method was used to analyze ores and concentrated solutions.

a. Procedure for the Determination of Iron Using Ortho-Phenanthroline

An aliquot of solution containing 0.01 to 0.2 mg of iron and having a low mineral acid content was transferred to a 25 ml volumetric flask. The volume of sodium acetate required to raise the pH to approximately 3.5 was then added. One ml of ten per cent hydroxalamine hydrochloride and one ml of ortho-phenanthroline (0.5 per cent) were added and the contents diluted to the mark. The transmittancy was determined within five to ten minutes.

b. Procedure for the Determination of Iron with the Flame Spectrophotometer[6]

The flame photometer was set at a wave length of 373.6 millimicrons and a slit width of 2.0 mm. An oxygen pressure of ten psig and hydrogen at four psig were used. A standard solution of 2000 ppm was used as 100 per cent intensity. The accuracy was found to be within five per cent.

Aliquots of the standard solution were diluted to obtain known concentrations and a calibration curve between 0 ppm iron and 2000 ppm iron was determined. When the samples were greater than 2000 ppm, an

aliquot was taken and diluted to give the desired range. The pH was adjusted to 1.0 or 2.0. In this range the variation of the flame intensity was very low.

3. Copper Determination

The quantity of copper was determined by the iodometric method[12] and also with the flame spectrophotometer. These methods are rapid and accurate when copper is in solution.

a. Procedure for the Determination of Copper Using the Beckman Flame Spectrophotometer[6]

The flame spectrophotometer was used at a wave length of 325 millimicrons and a slit width of 1.6 mm. The oxygen pressure was set at ten psig and the hydrogen at four psig. A standard solution of 1000 parts per million of cupric ion was used as 100 per cent flame intensity. A calibration chart was determined experimentally for use in analyzing unknowns.

4. Phosphate Determination[8]

The phosphate ion concentration was determined by the phosphate yellow method.[8] An aliquot of the sample was pipetted into a 100 ml volumetric flask and diluted to 50 ml. Twenty-five ml of phosphate reagent was then added and the contents of the flask was diluted to the 100 ml mark and read on the spectrophotometer at 425 millimicrons against a blank containing no phosphorous. The per cent of phosphate was determined from a previously prepared calibration curve.

5. Determination of pH Values

The pH values of the various solutions were determined with a

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[12] I. M. Kolthoff and E. B. Sandell, Textbook of Quantitative Inorganic Analysis, 3rd Ed., Macmillan Co., New York, 1953, p. 600.

Beckman pH meter.

6. Preparation of Special Reagents

a. Molybdenum Determination

Stannous Chloride. - One hundred grams of reagent grade dihydrate stannous chloride was placed in a one liter volumetric flask. To this eighty-seven and one-half milliliters of concentrated hydrochloric acid was added and the contents heated nearly to boiling. Hot distilled water was added to bring the volume to one liter. The solution was allowed to cool to room temperature and if the solution was not entirely clear the solution was filtered. This solution must be prepared fresh biweekly.

Butyl Acetate. - Reagent grade butyl acetate was cleaned and saturated by shaking and extracting 200 ml of butyl acetate with 20 ml of NaCNS and 30 ml of $SnCl_2$ in a separatory funnel. The lower layer was discarded and the process repeated until the butyl acetate showed no turbidity.

b. Phosphate Determination Reagent

Forty grams of ammonium molybdate was dissolved in water. To this one gram of ammonium vanadate was added and dissolved and then 200 ml of concentrated HNO_3 was added. The contents were diluted to one liter.

CHAPTER IV

RESULTS

A. Biological Oxidation of Molybdenite Concentrate

Two percolators were charged with 100 grams of Ottawa sand and 5 grams of molybdenite concentrate. One hundred ml of nutrient No. I was added and the percolators were sterilized in the autoclave. These two percolators were then placed in the bank side by side and attached to the same air supply. One percolator was inoculated with microorganisms from the leaching streams of Bingham Canyon which was called culture No. I, while the other served as a sterile control. The nutrient solution for the refill of the percolators was sterilized in the autoclave. Table VII and Figure 6 give the results of this study. These data show that there

TABLE VII

BIOLOGICAL OXIDATION OF MOLYBDENITE

Time In Days	Inoculated Cumulative Soluble Mo (mg)	Sterile Cumulative Soluble Mo (mg)
7	3.3	1.56
14	7.5	2.0
21	10.0	2.5
28	12.5	2.9
35	15.5	3.1
42	18.0	3.2
49	19.75	3.3

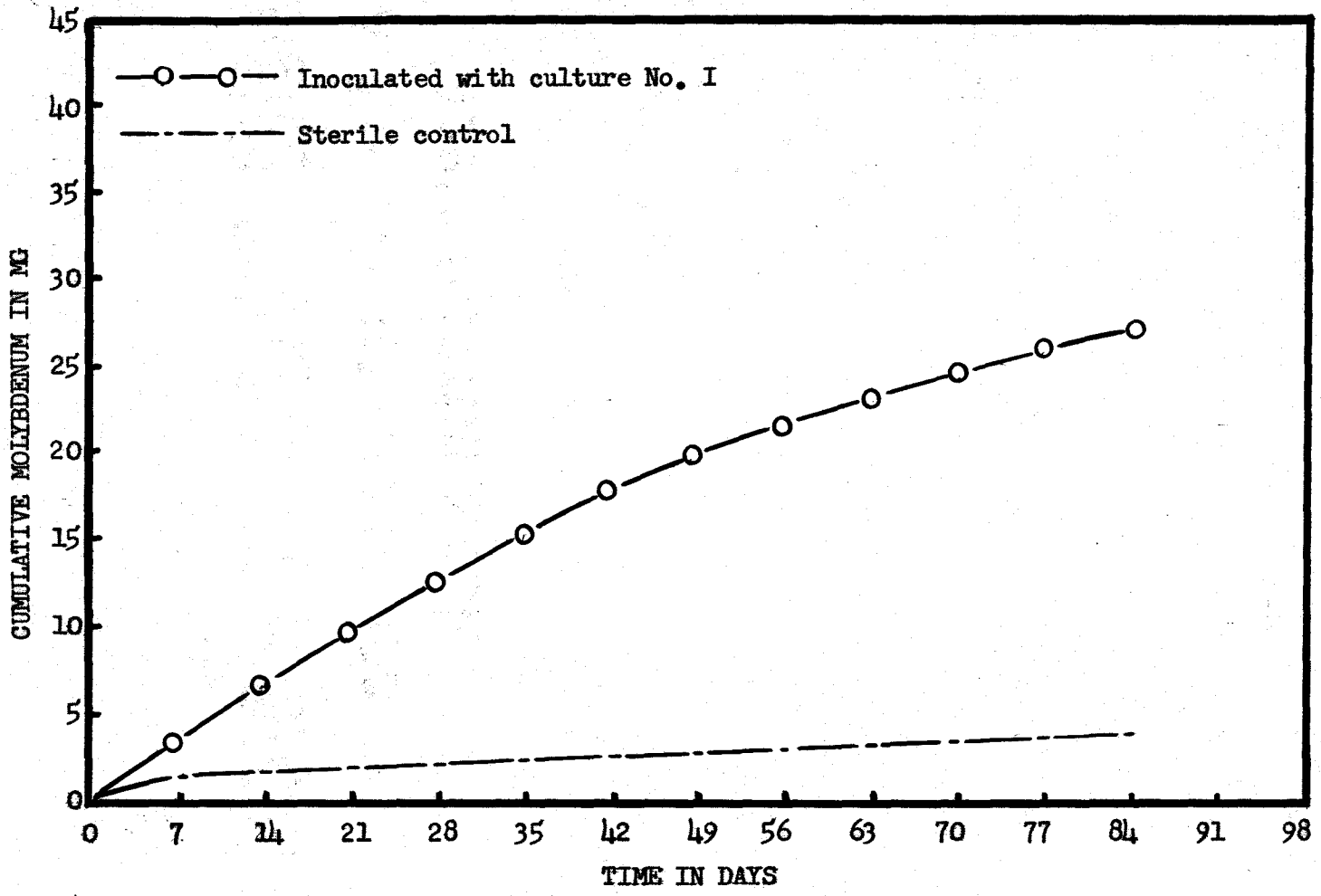

Fig. 6 The biological oxidation of molybdenite concentrate.

TABLE VII-Continued

Time In Days	Inoculated Cumulative Soluble Mo (mg)	Sterile Cumulative Soluble Mo (mg)
56	21.20	3.4
63	23.4	3.5
70	24.2	3.6
77	26.2	3.7
84	27.3	3.8

was approximately seven times more soluble molybdenum formed by bacterial action than under sterile conditions.

B. Biological Oxidation of Molybdenite Concentrate Mixed with Pyrite

Three percolators were charged with 5 grams of molybdenite concentrate and 5 grams of pyrite No. II along with the sand as previously described. Two were filled with 100 ml of nutrient No. I and inoculated with culture No. I, while the other was autoclaved for a sterile control. The results are given in Table VIII and Figure 7. These data show that

TABLE VIII

BIOLOGICAL OXIDATION OF MOLYBDENITE CONCENTRATE MIXED WITH PYRITE

	Number One		Number Two		Sterile	
Time In Days	Cumulative Mo (mg)	Cumulative Fe (mg)	Cumulative Mo (mg)	Cumulative Fe (mg)	Cumulative Mo (mg)	Cumulative Fe (mg)
7	1.51	8	1.0	8	1.51	1.0
14	4.51	172	9.4	364	2.06	3.0
21	14.51	627	27.4	834	2.56	4.5
28	26.51	1207	48.2	1304	2.96	6.0

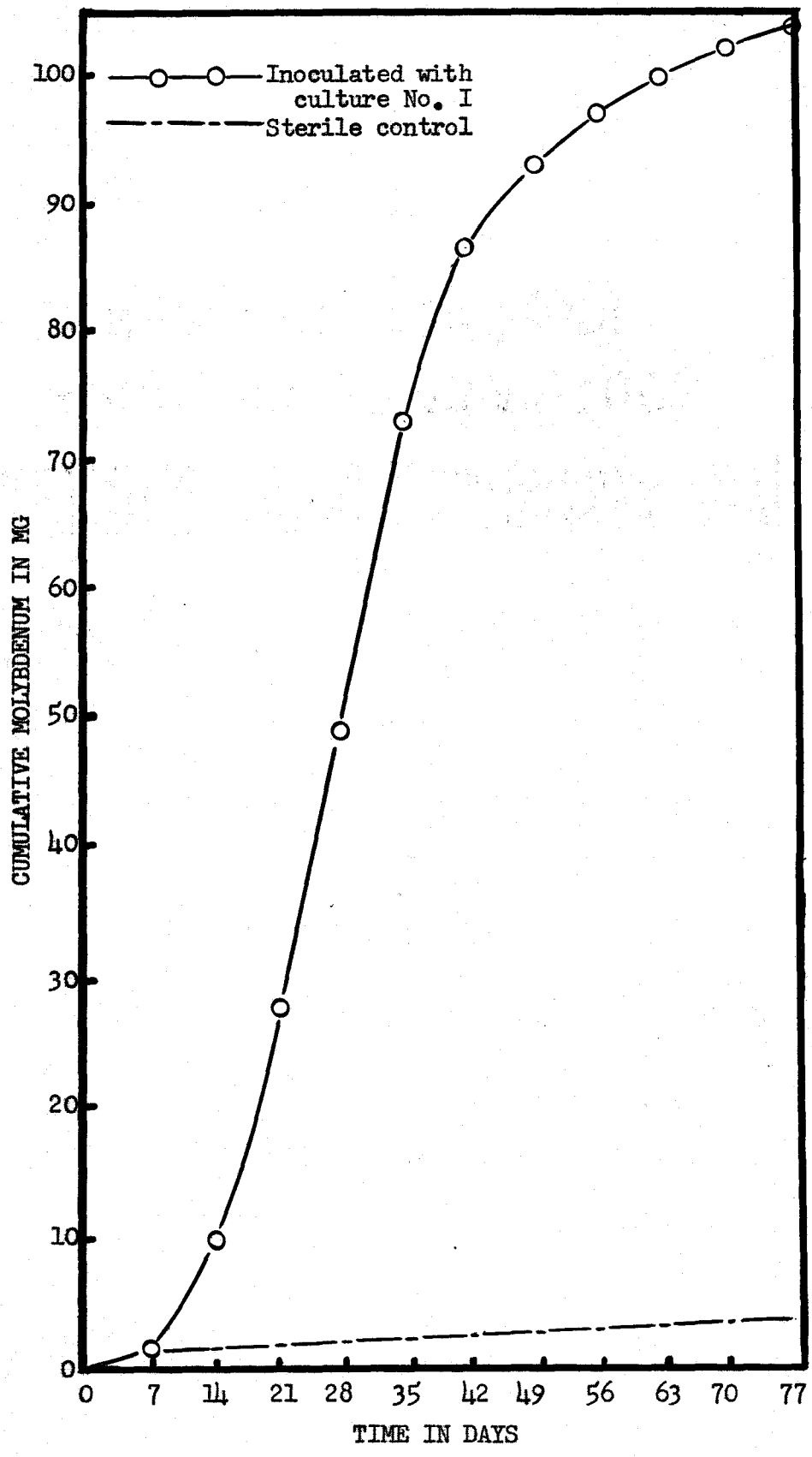

Fig. 7 Biological oxidation of pyrite mixed with molybdenite concentrate.

TABLE VIII-Continued

Time In Days	Number One Cumulative Mo (mg)	Number One Cumulative Fe (mg)	Number Two Cumulative Mo (mg)	Number Two Cumulative Fe (mg)	Sterile Cumulative Mo (mg)	Sterile Cumulative Fe (mg)
35	59.71	1629	72.6	1599	3.16	7.2
42	72.01	1869	86.3	1757	3.26	8.2
49	80.11	2003	93.62	1793	3.36	9.0
56	82.51	2055	97.12	1873	3.46	10.0
63	87.31	2125	100.12	1897	3.50	10.8
70	91.46	2165	102.27	1905	3.55	11.9
77	93.21	2195	103.42	1913	3.59	13.0

there was approximately 29 times more soluble molybdenum formed in the inoculated percolators than in the sterile control.

C. Biological Oxidation of Molybdenite Concentrate Mixed with Chalcopyrite

Two percolators were charged and set up in the same manner as in the preceding study. Five grams of chalcopyrite No. II was mixed with 5 grams of molybdenite concentrate and Ottawa sand. One percolator was inoculated with culture No. I while the other was kept as a sterile control. The results are given in Table IX and Figure 8. These data

TABLE IX

BIOLOGICAL OXIDATION OF CHALCOPYRITE AND MOLYBDENITE MIXTURE

Time In Days	Inoculated Cumulative Mo (mg)	Inoculated Cumulative Fe (mg)	Inoculated Cumulative Cu (mg)	Sterile Cumulative Mo (mg)	Sterile Cumulative Fe (mg)	Sterile Cumulative Cu (mg)
7	.5	21	32	.5	12	1.25
14	2.07	109	58	1.0	15	1.5
21	8.37	219	82	2.0	27	4.0

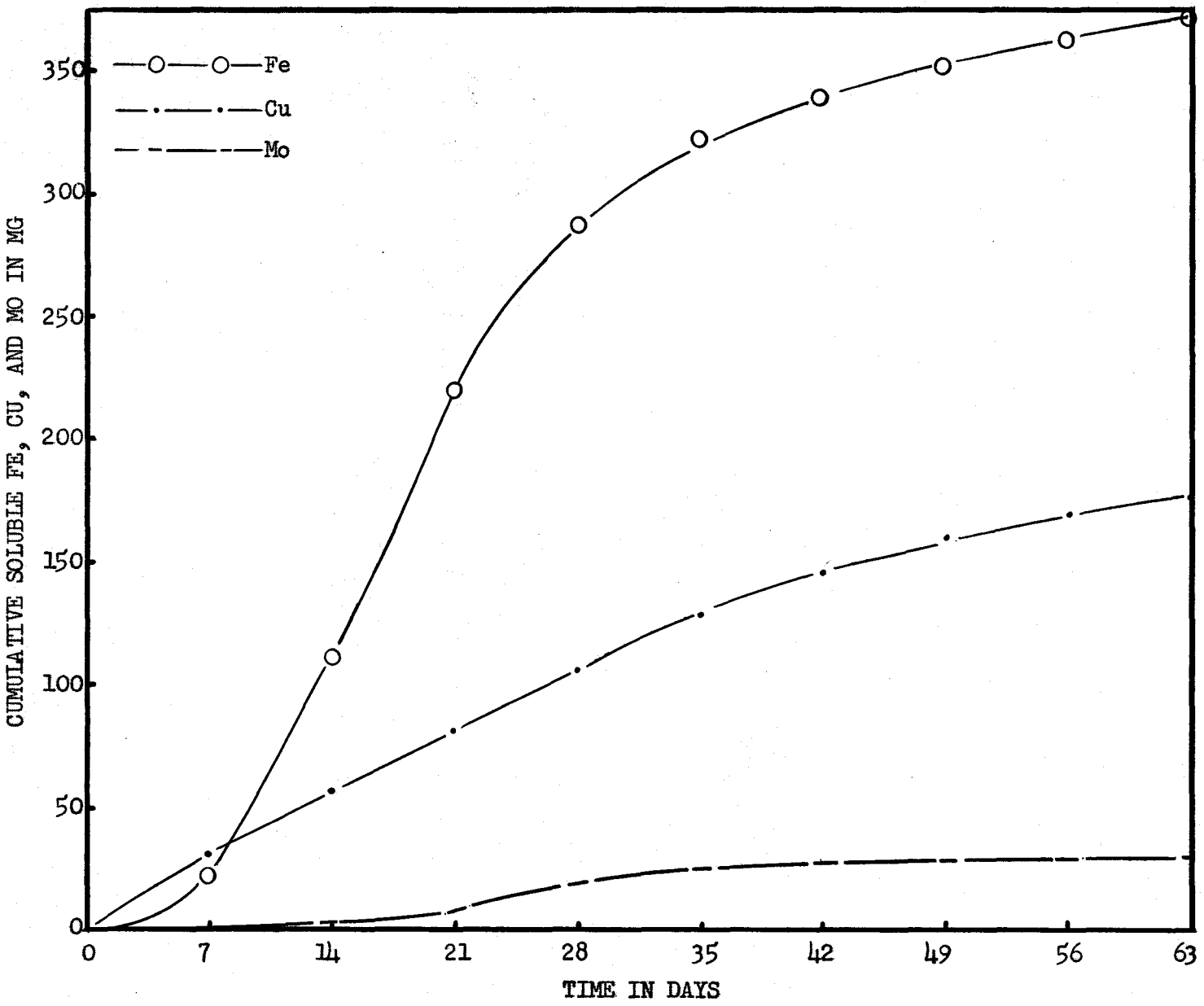

Fig. 8 The biological oxidation of chalcopyrite and molybdenite concentrate.

TABLE IX-Continued

Time In Days	Inoculated			Sterile		
	Cumulative Mo (mg)	Cumulative Fe (mg)	Cumulative Cu (mg)	Cumulative Mo (mg)	Cumulative Fe (mg)	Cumulative Cu (mg)
28	18.37	287	106	2.3	57	6.0
35	25.87	323	128	2.4	63	7.0
42	27.92	339	144	3.45	66	9.0
49	28.92	351	160	3.5	67	10.0
56	29.77	363	168	3.7	69	11.0
63	30.47	373	176	3.8	70	12.0

indicate that there may be a preferential oxidation of the chalcopyrite over the molybdenite.

D. Biological Oxidation of a Mixture of Molybdenite Concentrate and High Copper Pyrite

To check the possibility of the preferential oxidation of copper sulfides over molybdenite, fifteen percolators were set up as previously described and charged with 5 grams of pyrite No. V which has a copper content between the pyrite No. II and chalcopyrite No. II as shown in Table II. These results show that the copper sulfide was oxidized before the molybdenite. The concentration of the soluble copper dropped to about 40 ppm before the molybdenite underwent significant oxidation. These results are tabulated and plotted as a rate study in Table X and Figure 9. The same general trend was found in all 15 percolators, therefore, Table X and Figure 9 are given as a representative set of data. This further indicates the possibility of a preferential oxidation of copper sulfide over molybdenite.

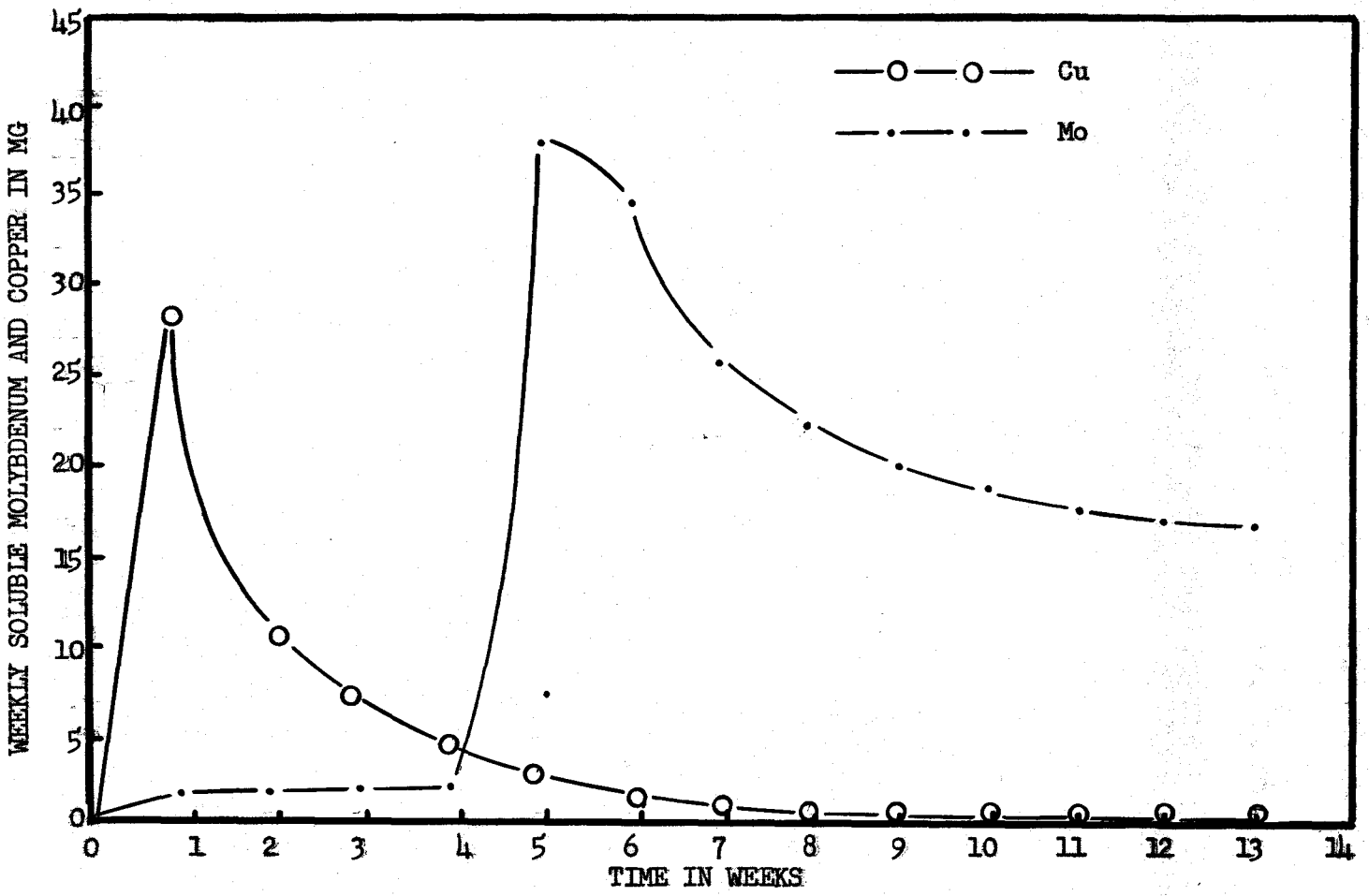

Fig. 9 The biological oxidation of a mixture of molybdenite concentrate and high copper pyrite.

TABLE X

BIOLOGICAL OXIDATION OF MOLYBDENITE CONCENTRATE AND HIGH COPPER PYRITE

Time In Weeks	Weekly Soluble Mo (mg)	Weekly Soluble Cu (mg)
1	2.0	28.0
2	2.5	11.5
3	3.0	7.5
4	3.2	4.8
5	38.0	3.0
6	34.5	1.5
7	26.5	1.0
8	23.0	0.9
9	21.5	0.8
10	21.0	0.7
11	20.5	0.6
12	19.5	0.5
13	19.2	0.5
14	--	--

E. A Rate Study on the Soluble Copper and Molybdenum Simultaneously Produced from Molybdenite Ore

A percolator was charged with 100 grams of molybdenite ore (composition given in Table II) to show the possibility of a preferential oxidation of the copper sulfides over the molybdenite. This percolator was then inoculated with culture No. II, drained weekly, analyzed for soluble copper and molybdenum, and refilled with fresh nutrient medium No. I. These results are tabulated in Table XI and represented

graphically in Figure 10.

TABLE XI

THE SOLUBLE COPPER AND MOLYBDENUM SIMULTANEOUSLY OXIDIZED FROM MOLYBDENITE ORE

Time In Weeks	Weekly Mo (mg)	Weekly Cu (mg)	Time In Weeks	Weekly Mo (mg)	Weekly Cu (mg)
1	1.5	1	12	8.1	8
2	1.6	53	13	8.5	6
3	1.5	68	14	9.7	4
4	1.5	78	15	8.6	3
5	1.5	88	16	8.4	1.5
6	1.4	67	17	10.2	1
7	1.5	56	18	8.3	0
8	1.8	46	19	9.3	0
9	3.9	34	20	9.7	0
10	5.9	20	21	10.4	0
11	7.3	12	22	10.4	0

The molybdenite ore had an initial copper content of 0.55 per cent. The time taken for the concentration of leached copper to reach 40 ppm was approximately eight weeks. At this time, 81 per cent of the copper in the original molybdenite ore had been solublized and there appeared to be significant oxidation of the molybdenite. At the end of the 17th week, 97.5 per cent of the copper in the molybdenite ore had been solublized. From this time until the completion of the investigation no more soluble copper was detected. The same general trend in all studies was found when the molybdenite was oxidized simultaneously with copper sulfide minerals.

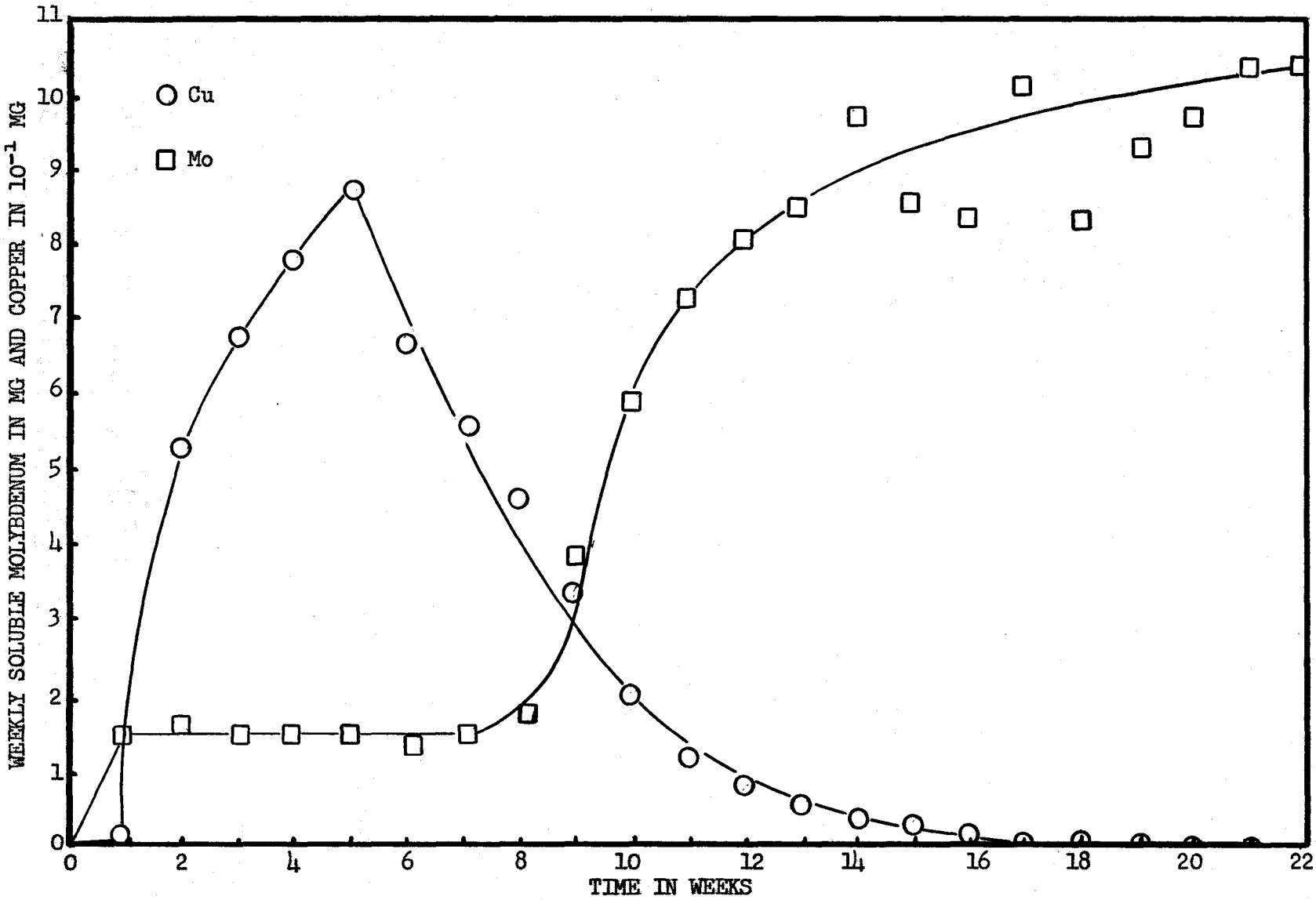

Fig. 10 The soluble copper and molybdenum simultaneously produced from molybdenite ore.

F. The Effect of Cupric Ion on the Biological Oxidation of Molybdenite

It was found in all cases that the concentration of soluble copper dropped to approximately 40 ppm before significant oxidation was observed upon the molybdenite. To determine whether it was the cupric ion in solution or preferential oxidation of the copper sulfide minerals that was preventing the molybdenite from being oxidized, a series of percolators were set up with different concentration of cupric ion from 0 to 75 ppm mixed in nutrient No. II. This concentration range was nearly double the critical concentration of 40 ppm. This study was run for a period of thirty-five days. The results are tabulated in Table XII and represented graphically in Figure 11. These data indicate there was no inhibitive effect of the cupric ion in the range studied upon the biological oxidation of molybdenite.

TABLE XII

THE EFFECT OF CUPRIC ION ON
THE BIOLOGICAL OXIDATION OF MOLYBDENITE

Cu^{++} Concentration (ppm)	Cumulative Mo (mg)
0	108.51
10	97.19
20	110.36
30	84.03
40	89.61
50	94.77
75	103.40

The reason for the preferential oxidation of the copper sulfide

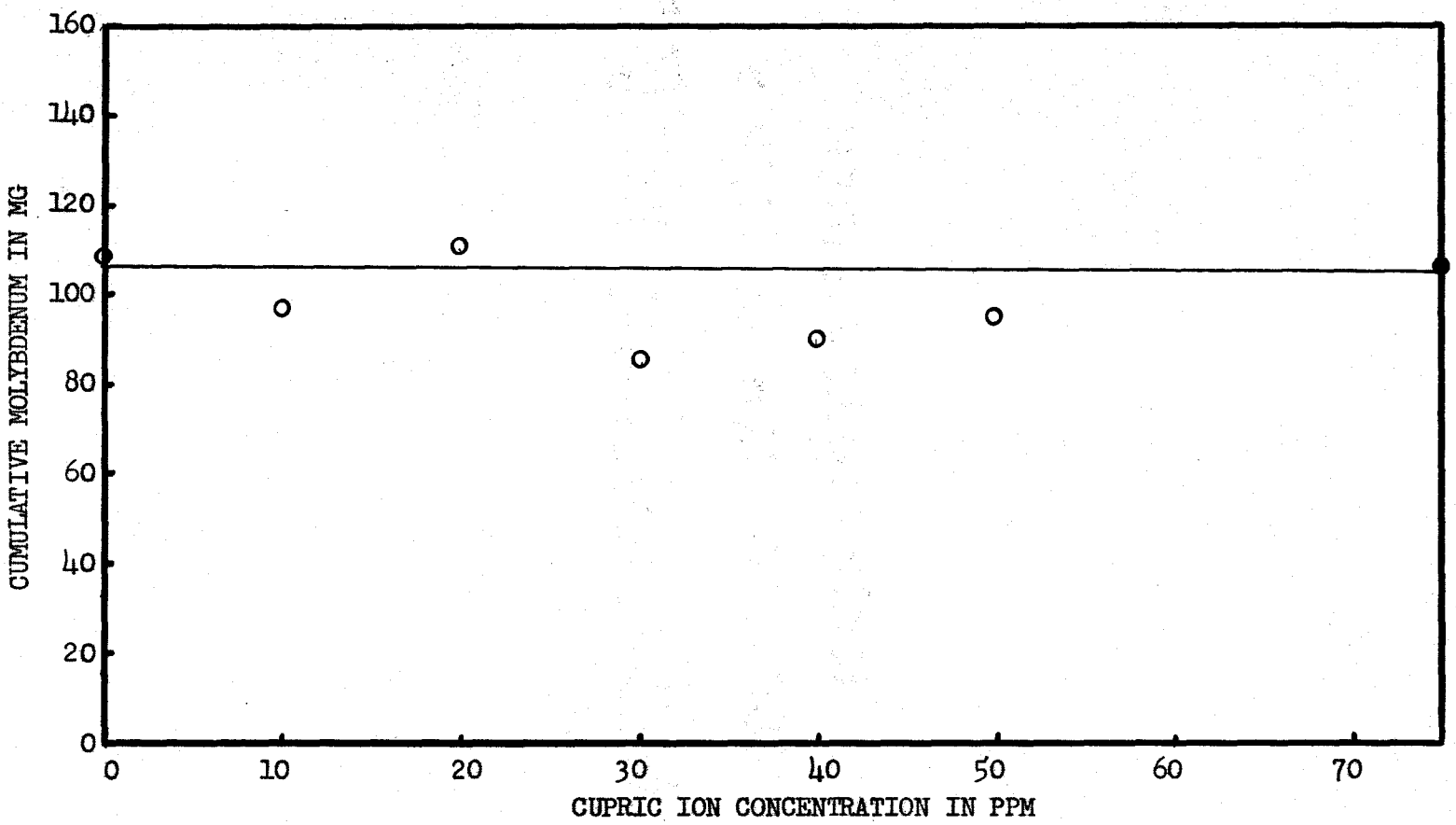

Fig. 11 The effect of cupric ion on the biological oxidation of molybdenite.

minerals over the molybdenite is not known. The presence of the cupric ion does not inhibit the oxidation of the molybdenite in the concentration ranges studied. The thermodynamics of the oxidation of the sulfide minerals show negative values for their free energy changes which indicate that the reactions are possible.[1,2] It may be due to the differences in the crystal structures of the sulfide minerals. The copper sulfides may be slightly more soluble than the molybdenite which may favor the oxidation of the copper sulfide minerals over the molybdenite.

G. The Result of Mixing Molybdate Ion with Fresh Bingham Canyon Stream Solution

The possibility of an insoluble molybdate being formed in the leaching streams of Bingham Canyon and precipitating out is a probable reason why such a small amount of soluble molybdenum was detected. To investigate this possibility, aliquots of fresh Bingham Canyon stream solution were mixed with solutions of molybdic acid, ammonium molybdate, and sodium molybdate to a final molybdate concentration of 1000 ppm. There was no precipitation, coagulation, or turbidity observed over a period of two days, even upon centrifugation by the three molybdenum compounds. The molybdate ion is also soluble in the presence of ferrous and ferric, cupric, and aluminum ions that have concentrations up to 7500 ppm at a pH of 1.75.

These results led to the conclusion that if there are components

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[1]N. A. Lange, Handbook of Chemistry, 8th Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1952.

[2]W. M. Latimer, Oxidation Potentials, 2nd Ed., Prentice-Hall, Inc., New York, 1952.

in solution in the Bingham Canyon leaching streams that would precipitate the molybdate ion they were undetectable. Thus it can be concluded that the soluble molybdenum is not precipitated in the leaching streams of Bingham Canyon. If the molybdenite content in the low grade ores in Bingham Canyon is being oxidized, it should be found in solution, providing the molybdenite is present in sufficient quantity in the waste rock dumps to be solublized.

H. The Effect of Particle Size on the Biological Oxidation of Molybdenite Ore

Four percolators were charged with molybdenite ore as follows: (A) with 100 grams crushed and screened between the limits of 10 to 30 mesh, (B) with 100 grams between the limits of 30 to 60 mesh, and (C) and (D) with 100 grams 60 mesh and greater. They were all sterilized in the usual manner and (A), (B), and (C) were inoculated with culture No. III while (D) was kept as a control. The results of this study are tabulated in Table XIII and Figure 12. They show that

TABLE XIII

THE BIOLOGICAL OXIDATION OF MOLYBDENITE ORE IN DIFFERENT PARTICLE SIZES
Cumulative Soluble Molybdenum in mg

Time In Days	Inoculated			Sterile
	10 to 30 Mesh	30 to 60 Mesh	60 & Greater Mesh	60 & Greater Mesh
7	0.5	0.8	2.5	1.5
14	2.1	2.4	4.1	2.0
21	3.1	3.8	6.9	2.5
28	4.6	5.3	8.4	2.9
35	5.65	7.05	10.15	3.1

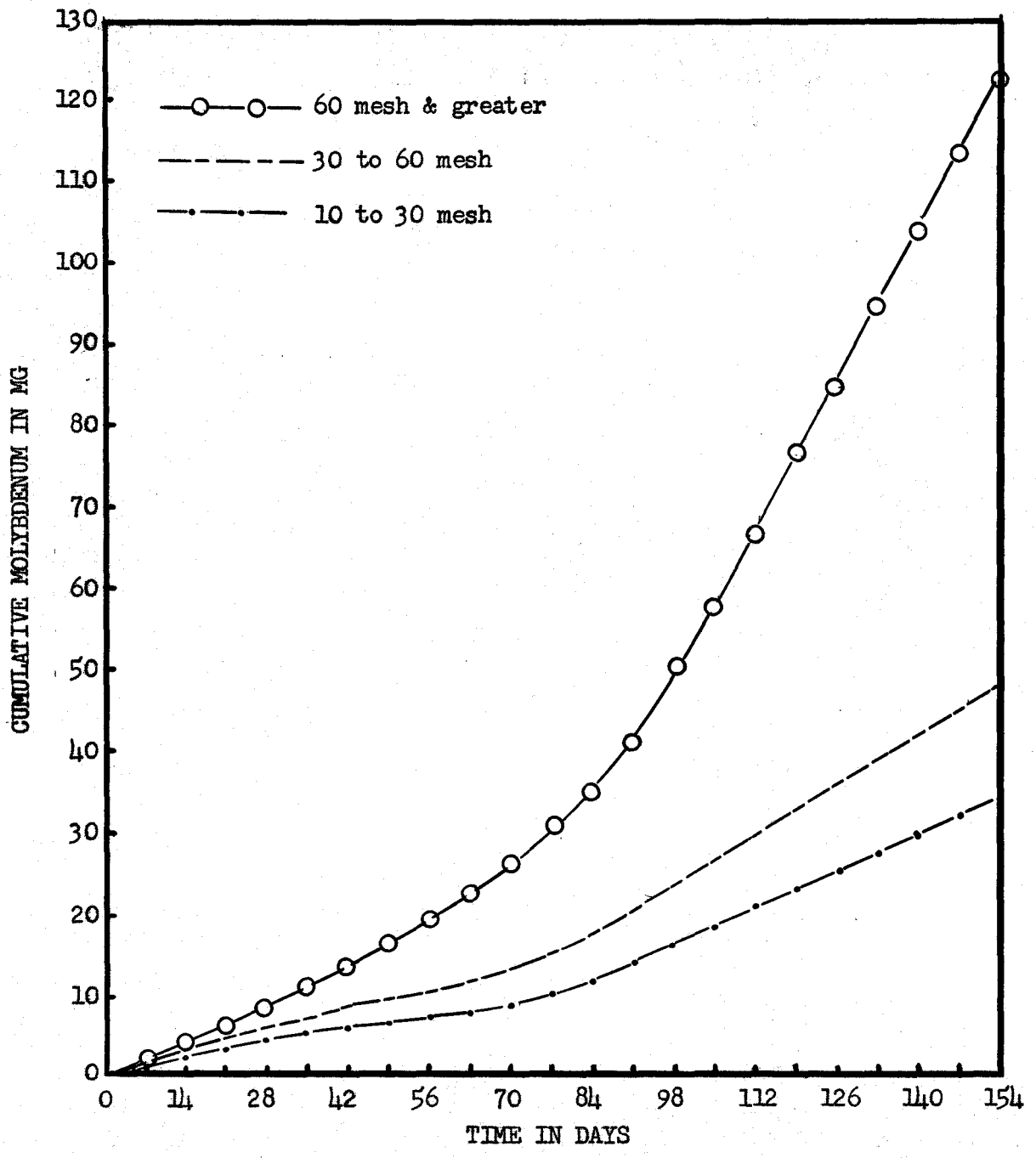

Fig. 12 The biological oxidation of molybdenite ore in different particle sizes.

TABLE XIII-Continued

Time In Days	Inoculated 10 to 30 Mesh	Inoculated 30 to 60 Mesh	Inoculated 60 & Greater Mesh	Sterile 60 & Greater Mesh
42	6.10	8.3	12.98	3.2
49	6.55	9.87	16.23	3.3
56	7.20	10.79	20.03	3.4
63	7.80	11.54	25.23	3.5
70	8.73	12.69	27.43	3.6
77	10.03	15.69	31.18	3.7
84	11.48	17.64	34.28	3.8
91	13.33	20.64	40.93	3.9
98	16.08	24.39	51.23	4.0
105	18.18	26.29	57.63	4.1
112	21.26	29.37	66.30	4.2
119	23.52	32.25	76.45	4.3
126	25.46	35.14	84.73	4.4
133	27.63	38.50	94.18	4.5
140	29.18	40.83	103.84	4.6
147	31.62	44.55	113.07	4.7
154	34.02	48.30	123.47	4.8

the amount of leaching is a function of the particle size and that the molybdenite ore may be oxidized by microorganisms. A decrease of the diameter in the range of two gave an increased oxidation of nearly fifty per cent. An approximate four-fold decrease in the diameter gave an oxidation increase of nearly 400 per cent.

I. The Effect of Pyrite on the Biological Oxidation of Molybdenite Concentrate

Four percolators were charged with 100 grams of Ottawa sand and 5 grams of molybdenite concentrate. In addition 5 grams of pyrite No. III was added to percolators (A) and (B) and all were sterilized. (A) and (C) were inoculated with culture No. I. The results of this study are tabulated in Table XIV and represented graphically in Figure 13.

TABLE XIV

THE EFFECT OF MIXING PYRITE WITH MOLYBDENITE CONCENTRATE
Cumulative Soluble Molybdenum in mg

Time In Days	Percolator A	Percolator B	Percolator C	Percolator D
7	2.07	1.5	3.5	1.5
14	6.57	2.0	7.5	2.0
21	8.62	2.5	12.5	2.5
28	15.12	2.9	17.1	2.9
35	51.12	3.1	21.5	3.1
42	80.52	3.2	31.5	3.2
49	106.72	3.3	37.75	3.3
56	122.97	3.4	42.35	3.4
63	137.97	3.5	46.93	3.5
70	152.42	3.6	51.13	3.6
77	162.62	3.7	54.88	3.7
84	185.47	3.8	58.08	3.8
91	198.37	3.9	61.00	3.9
98	215.06	4.0	63.28	4.0

These results indicate that there was an increase of approximately 350

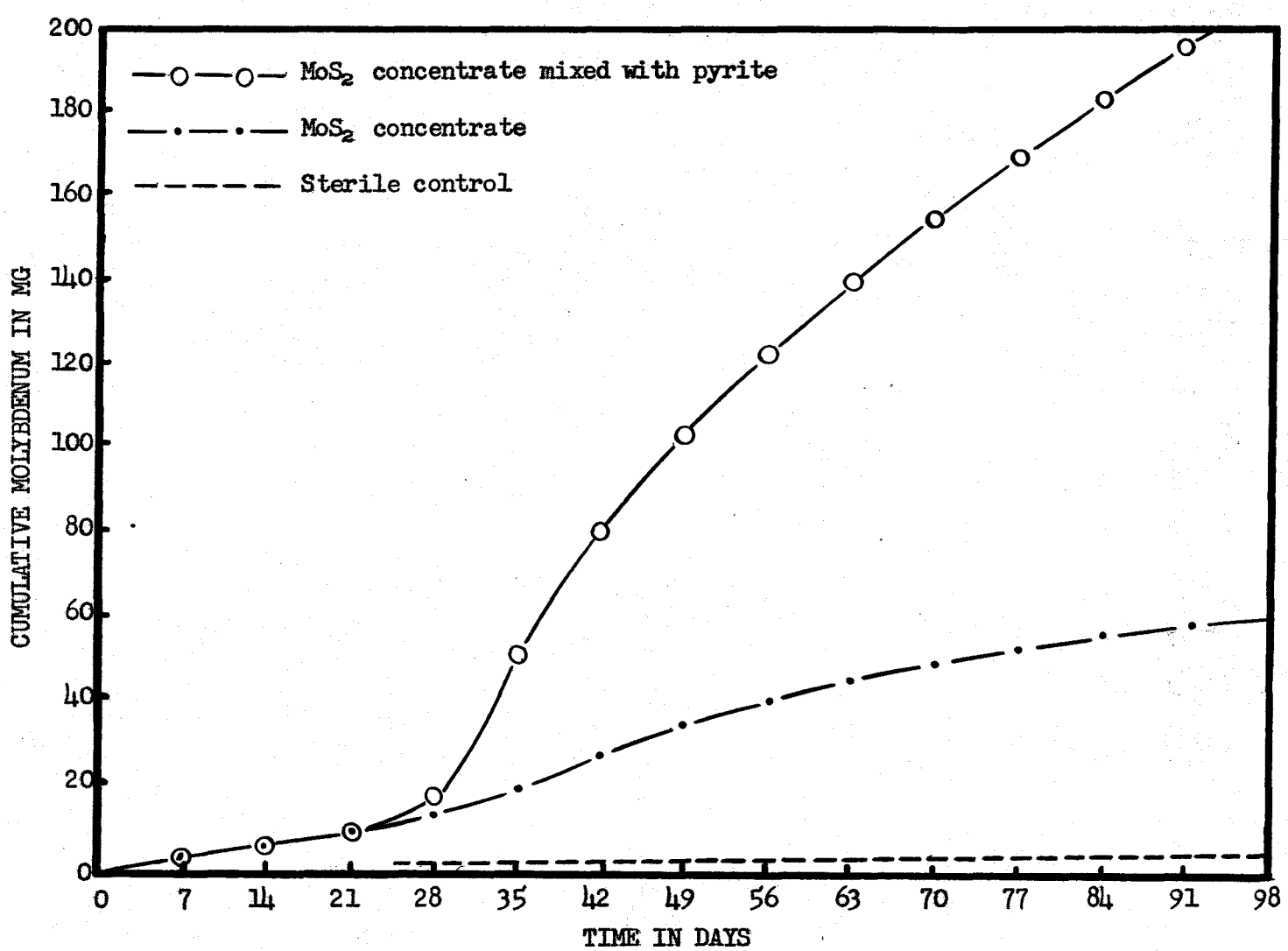

Fig. 13 The effect of pyrite on the biological oxidation of molybdenite concentrate.

per cent soluble molybdenum when pyrite was mixed with the molybdenite concentrate. There was no noticeable effect in the sterile control.

J. The Effect of Pyrite on the Biological Oxidation of Molybdenite Ore

Three percolators were charged with molybdenite ore that passed a 60 mesh sieve. Five grams of pyrite No. III was added to percolators (A) and (B). All three along with their charges were sterilized. (B) and (C) were then inoculated with culture No. III while (A) served as a control. The results are given in Table XV and Figure 14. These data

TABLE XV

THE BIOLOGICAL OXIDATION OF MOLYBDENITE ORE MIXED WITH PYRITE
Cumulative Soluble Molybdenum in mg

Time In Days	Percolator A	Percolator B	Percolator C
7	1.5	0.3	2.5
14	2.0	1.9	4.1
21	2.5	3.4	6.9
28	2.9	4.9	8.4
35	3.1	6.65	10.15
42	3.2	7.65	12.98
49	3.3	16.85	16.23
56	3.4	24.35	20.03
63	3.5	32.45	25.23
70	3.6	45.45	27.43
77	3.7	56.75	31.18
84	3.8	67.25	34.28
91	3.9	73.25	40.93
98	4.0	80.05	51.23
105	4.1	94.35	57.63

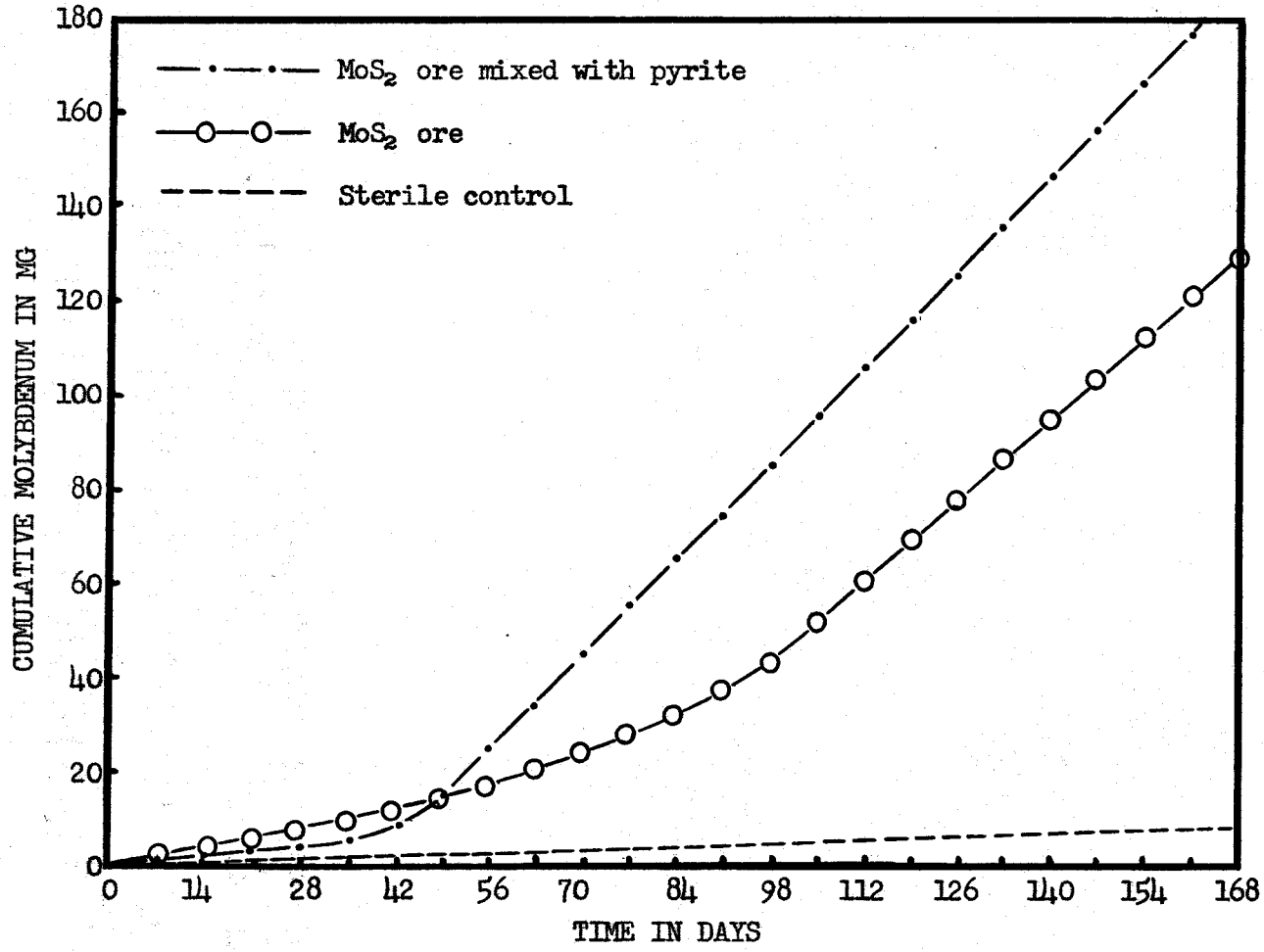

Fig. 14 The effect of pyrite on the biological oxidation of molybdenite ore.

indicate that there was approximately 45 per cent more molybdenum solubilized when pyrite was mixed with the molybdenite ore. Possibly the reason this is more significant with the molybdenite concentrate than with the molybdenite ore is because of the absence of iron in the molybdenite concentrate.

K. The Effect of Ferrous Iron on the Biological Oxidation of Molybdenite Concentrate

The results in the preceding study indicated the presence of iron increased the activity on the biological oxidation of molybdenite. An investigation was conducted to see if the presence of ferrous iron in the nutrient medium would have an effect on the biological oxidation.

A series of percolators were set up in the usual manner and charged with 5 grams of molybdenite concentrate. The nutrient medium No. II was made up and ferrous iron ($FeSO_4 \cdot 7H_2O$) was added in variable amounts as shown in Table XVI. The soluble molybdenum produced at each concentration of ferrous iron was determined weekly and recorded for a period of six weeks. The results are given in Table XVI and Figure 15.

TABLE XVI

THE EFFECT OF FERROUS IRON ON THE BIOLOGICAL OXIDATION OF MOLYBDENITE CONCENTRATE

Fe^{++} Concentration (ppm)	Cumulative Mo in mg
0	21.73
25	24.48
50	27.74
100	29.29
150	32.00

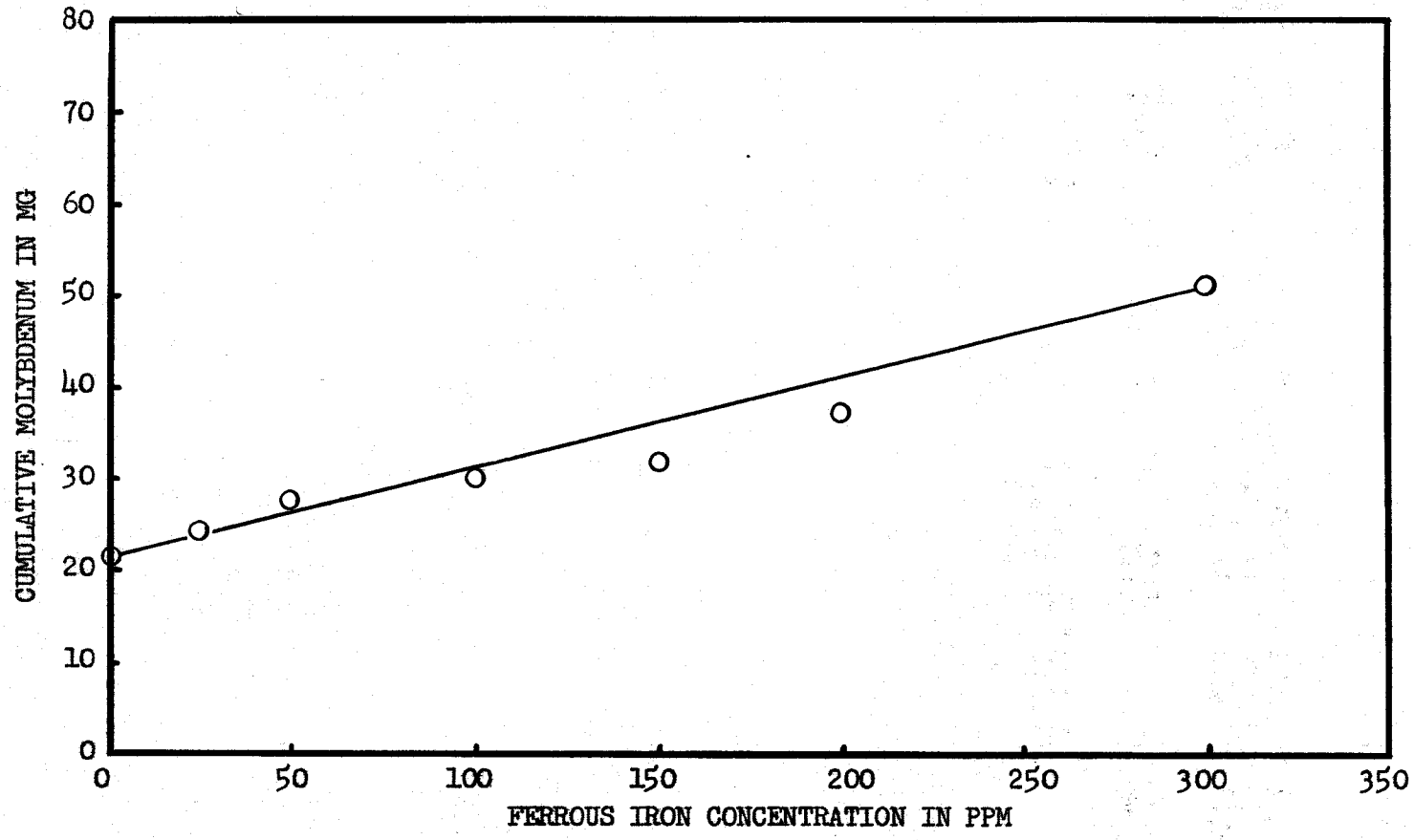

Fig. 15 The effect of ferrous iron on the biological oxidation of molybdenite concentrate.

TABLE XVI-Continued

Fe^{++} Concentration (ppm)	Cumulative Mo in mg
200	37.42
300	51.03

These data show there is an increased activity in the presence of ferrous iron on the biological oxidation of molybdenite. No optimum was determined with the ferrous iron concentration used in this investigation.

L. The Effect of Bacterial Transfer on the Oxidation of Molybdenite Concentrate

Culture No. II was transferred to duplicate percolators as those described in topic A. They were transferred the sixth week which was approximately at their highest activity. The results are given in Table XVII and Figure 16. These data show that more efficient leaching can be

TABLE XVII

THE EFFECT OF BACTERIAL TRANSFER ON THE OXIDATION OF MOLYBDENITE CONCENTRATE
Cumulative Molybdenum in mg

Time In Days	Transfer No. 1 (A)	Transfer No. 1 (B)	Initial
7	3.6	3.5	3.3
14	6.0	7.5	7.5
21	9.6	12.5	10.0
28	14.2	17.1	12.5
35	19.3	21.8	15.5
42	29.0	31.8	18.0

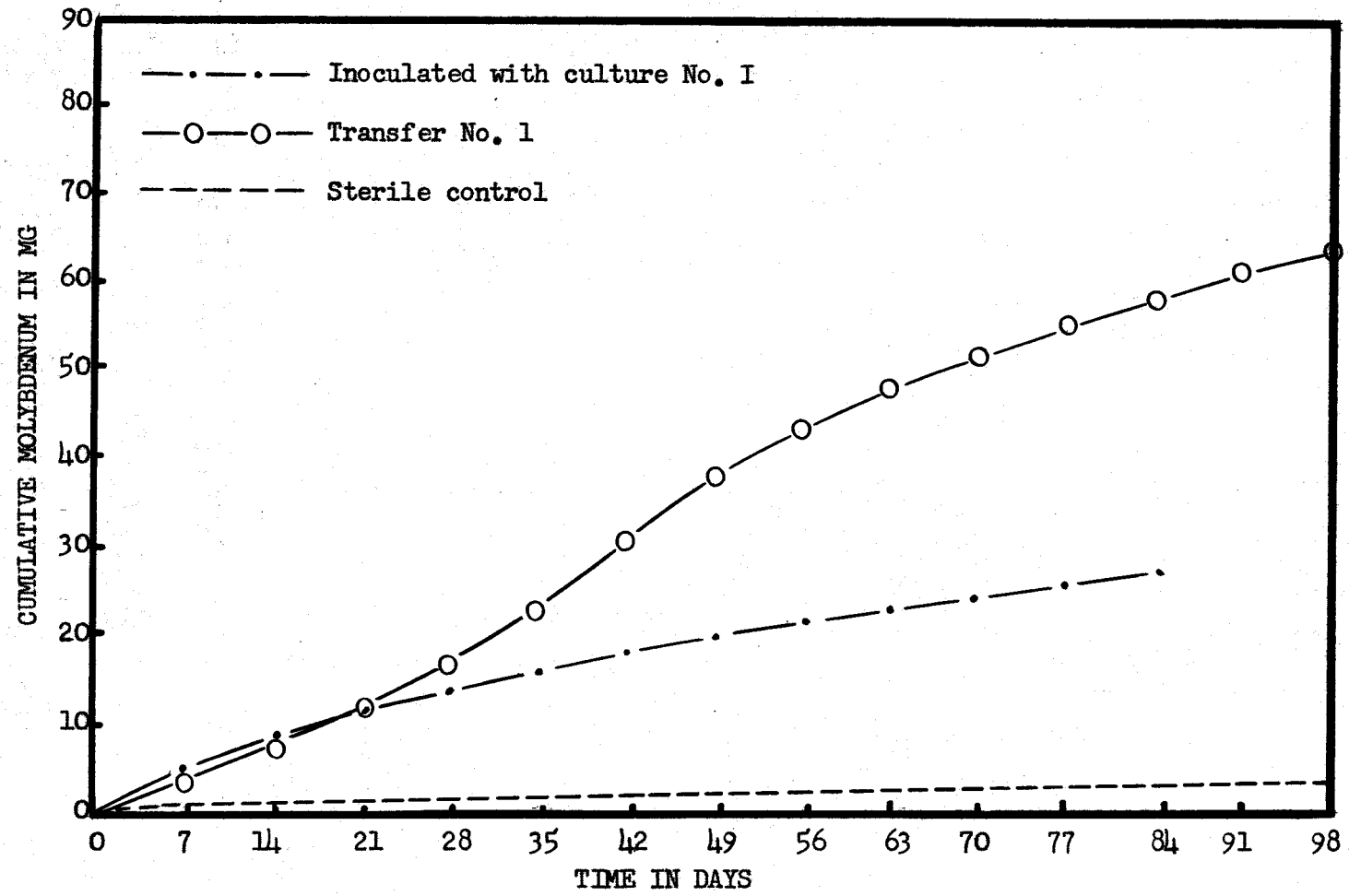

Fig. 16 The effect of bacterial transfer on the oxidation of molybdenite concentrate.

TABLE XVII-Continued

Time In Days	Transfer No. 1 (A)	Transfer No. 1 (B)	Initial
49	35.2	38.05	19.75
56	40.0	42.65	21.20
63	44.6	47.23	23.4
70	49.8	51.43	24.2
77	53.05	55.28	26.2
84	56.35	58.28	27.3
91	59.05	61.40	--
98	60.80	63.68	--

attained by enrichment of the culture by repeated transfers. The results of percolator (B) are plotted as representative for the transfer shown in Figure 16.

M. The Effect of Bacterial Transfer on the Oxidation of Molybdenite Concentrate Mixed with Pyrite

Culture No. III at the fifth week was transferred to a freshly prepared duplicate percolator of those described in topic B. These results are shown in Table XVIII and Figure 17 for this transfer and a second transfer under the same conditions. These data further support the results of the preceding study.

N. The Oxidized States of Soluble Molybdenum Formed in the Biological Oxidation of Molybdenite

It was reported in Table VI of Chapter III that all of the oxidized soluble molybdenum was either in the pentavalent or hexavalent state. The relative amounts of the two oxidized states of molybdenum

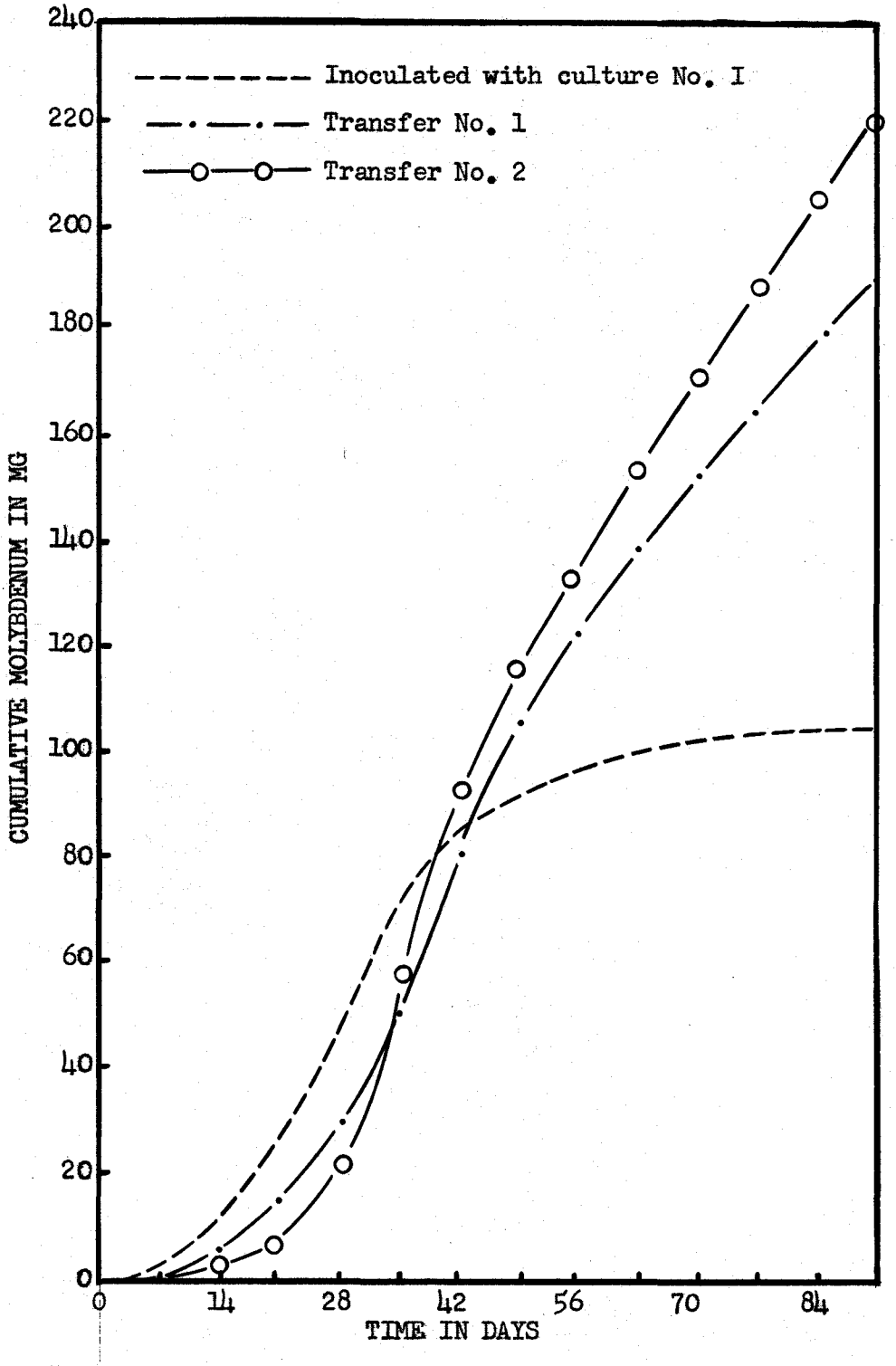

Fig. 17 The effect of bacterial transfer on the oxidation of molybdenite concentrate mixed with pyrite.

TABLE XVIII

THE EFFECT OF BACTERIAL TRANSFER ON THE OXIDATION OF MOLYBDENITE CONCENTRATE MIXED WITH PYRITE
Cumulative Molybdenum in mg

Time In Days	Initial	Transfer No. 1	Transfer No. 2
7	1.0	2.10	1.72
14	9.4	5.85	3.57
21	27.4	7.25	5.37
28	48.2	22.45	21.37
35	72.6	61.05	58.97
42	86.3	89.39	93.37
49	93.62	111.95	111.37
56	97.12	127.35	132.67
63	100.12	142.85	152.07
70	102.27	158.35	171.72
77	103.42	163.78	182.32
84	104.3	174.13	205.42
91	105.1	183.78	222.02

were determined by using the butyl acetate extraction of the pentavalent molybdenum thiocyanate complex. An aliquot of sample was taken and the pentavalent molybdenum was extracted with fresh reagent butyl acetate without using any stannous chloride to reduce the hexavalent molybdenum. The absorbancy of the extract was then determined. The total amount of molybdenum in the solution was then found. The amount of pentavalent molybdenum was subtracted from the total to determine the quantity in the hexavalent state. Table XIX gives a number of samples at different intervals of the study to determine the relative percentage in the two

valence states. The average amount of molybdenum found in the pentavalent

TABLE XIX

THE RELATIVE AMOUNTS OF THE OXIDIZED SOLUBLE STATES OF MOLYBDENUM FORMED IN THE OXIDATIVE PROCESS

Total Soluble Mo (mg) in 100 ml of Percolator Drain	Weight In Pentavalent State (mg)	Weight In Hexavalent State (mg)	Per Cent Pentavalent	Per Cent Hexavalent
20	3.82	16.18	19.1	80.1
16.3	3.095	13.205	19.0	81.0
18.1	3.45	14.65	19.05	80.95
23.2	4.40	18.8	18.95	81.05
21.2	4.07	17.13	19.2	80.8
12.0	2.275	9.725	18.97	81.03
8.3	1.58	6.72	19.02	80.98
15.8	3.00	12.8	18.98	81.02
19.6	3.73	15.87	19.04	80.96

state was 19.1 per cent and in the hexavalent state was 80.9 per cent.

The preceding results and those reported in Table VI of Chapter III indicate that the reaction is not a metathesis reaction, but is an actual oxidation of the molybdenite. The oxidation state of the molybdenum in molybdenite is plus 4 while that found in solution was either plus 5 or plus 6. The reaction may be assumed to proceed as follows:

$$2MoS_2 + 19/2\ O_2 + 8H^+ \longrightarrow Mo_2O_5 \cdot XH_2O + 4H_2SO_4$$

$$Mo_2O_5 \cdot XH_2O + 1/2\ O_2 \longrightarrow 2MoO_3 \cdot H_2O + (X-2)H_2O$$

The hydrated state of molybdenum trioxide in a water solution is commonly known as molybdic acid, H_2MoO_4.

O. The Acidity Produced by the Biological Oxidation of Molybdenite Concentrate

The results of the preceding investigation showed that when the molybdenite was oxidized two acids were formed, so a study of the pH versus time of oxidation in hours was determined. The results of this investigation are recorded in Table XX and in Figure 18.

TABLE XX

THE ACIDITY PRODUCED BY THE BIOLOGICAL OXIDATION OF MOLYBDENITE CONCENTRATE

Time In Hours	pH	Time In Hours	pH
0	2.28	72	2.11
12	2.24	96	2.075
24	2.20	120	2.04
36	2.18	144	2.01
48	2.15	192	1.97
60	2.13	288	1.93

The percolators were started in the usual manner and filled with 150 ml of No. II nutrient solution. The electrodes of the pH meter were placed inside the percolator resting in the solution. At the desired time interval the pH was checked and recorded. The pH values showed a steady decrease. The steady decrease of the pH gives an indication of the two acids being formed, molybdic and sulfuric acids. The intial pH of the percolator is lower than 2.65 due to the acid content from the preceding drain.

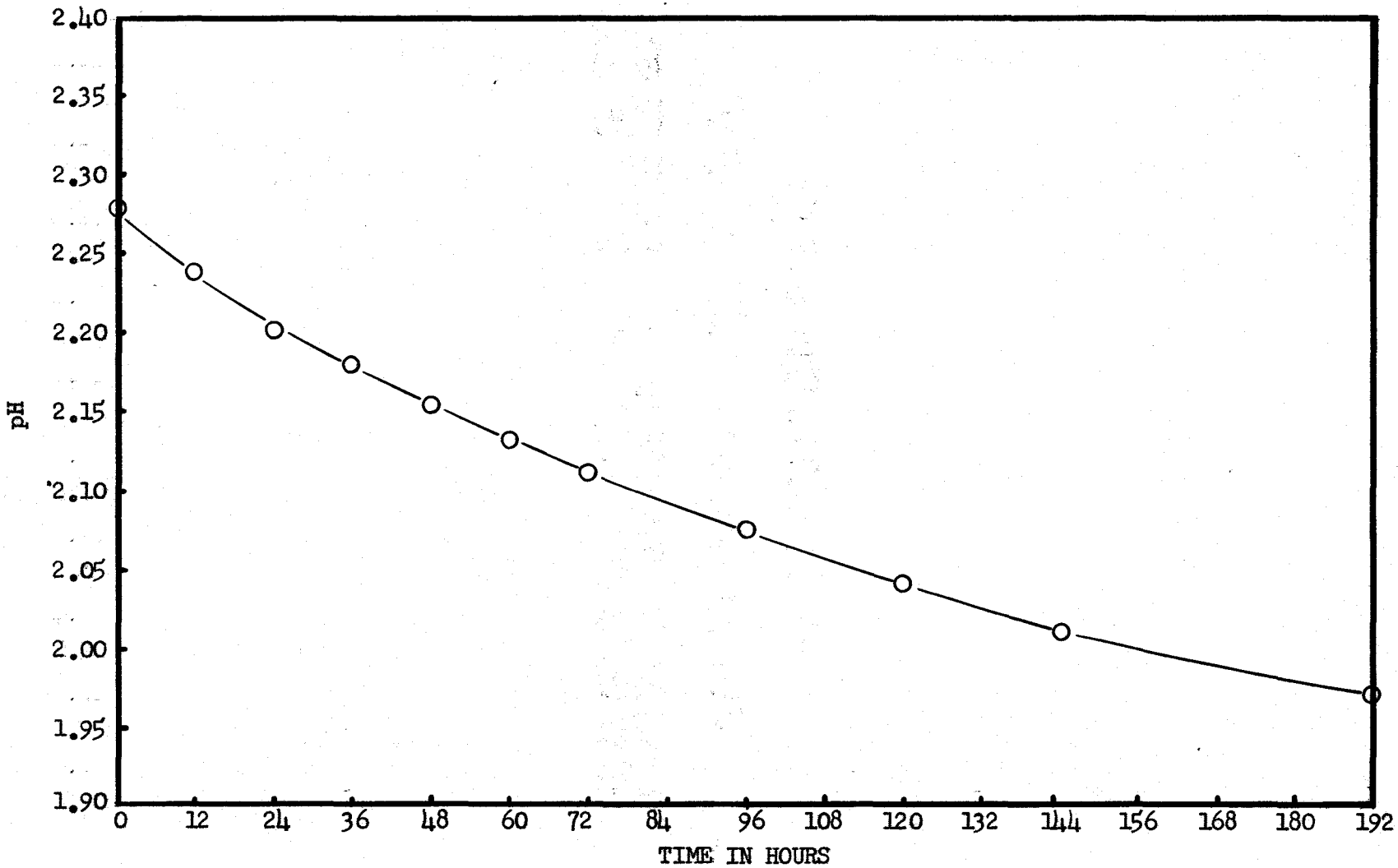

Fig. 18 The acidity produced by the biological oxidation of molybdenite concentrate.

P. The Acidity Produced by the Biological Oxidation of Molybdenite Concentrate Mixed with Pyrite

A study similar to that described in topic O, only that 5 grams of pyrite No. IV was mixed with the molybdenite concentrate, was carried out. The results shown in Table XXI and Figure 19 indicate that the same qualitative results are obtained but are more significant because part of the acidity is due to the oxidation of the pyrite and its effect on the oxidation of the molybdenite.

TABLE XXI

THE ACIDITY PRODUCED BY THE BIOLOGICAL OXIDATION OF MOLYBDENITE CONCENTRATE MIXED WITH PYRITE

Time In Hours	pH	Time In Hours	pH
0	2.5	72	1.52
12	2.10	96	1.46
24	1.90	120	1.32
36	1.78	144	1.26
48	1.67	192	1.20
60	1.59	288	1.15

Q. Percentage of Molybdenum Solublized from Molybdenite Ore

It was desired to find the percentage of the molybdenum that could be solublized from the molybdenite ore by biological oxidation. A percolator to contain 100 grams of molybdenite ore mixed with pyrite No. II and another percolator to contain 100 grams of molybdenite ore were charged, inoculated, drained weekly, and analyzed for the amount of soluble molybdenum. The molybdenite ore was crushed to 60 mesh or finer in this investigation. These two percolators were run for a period of

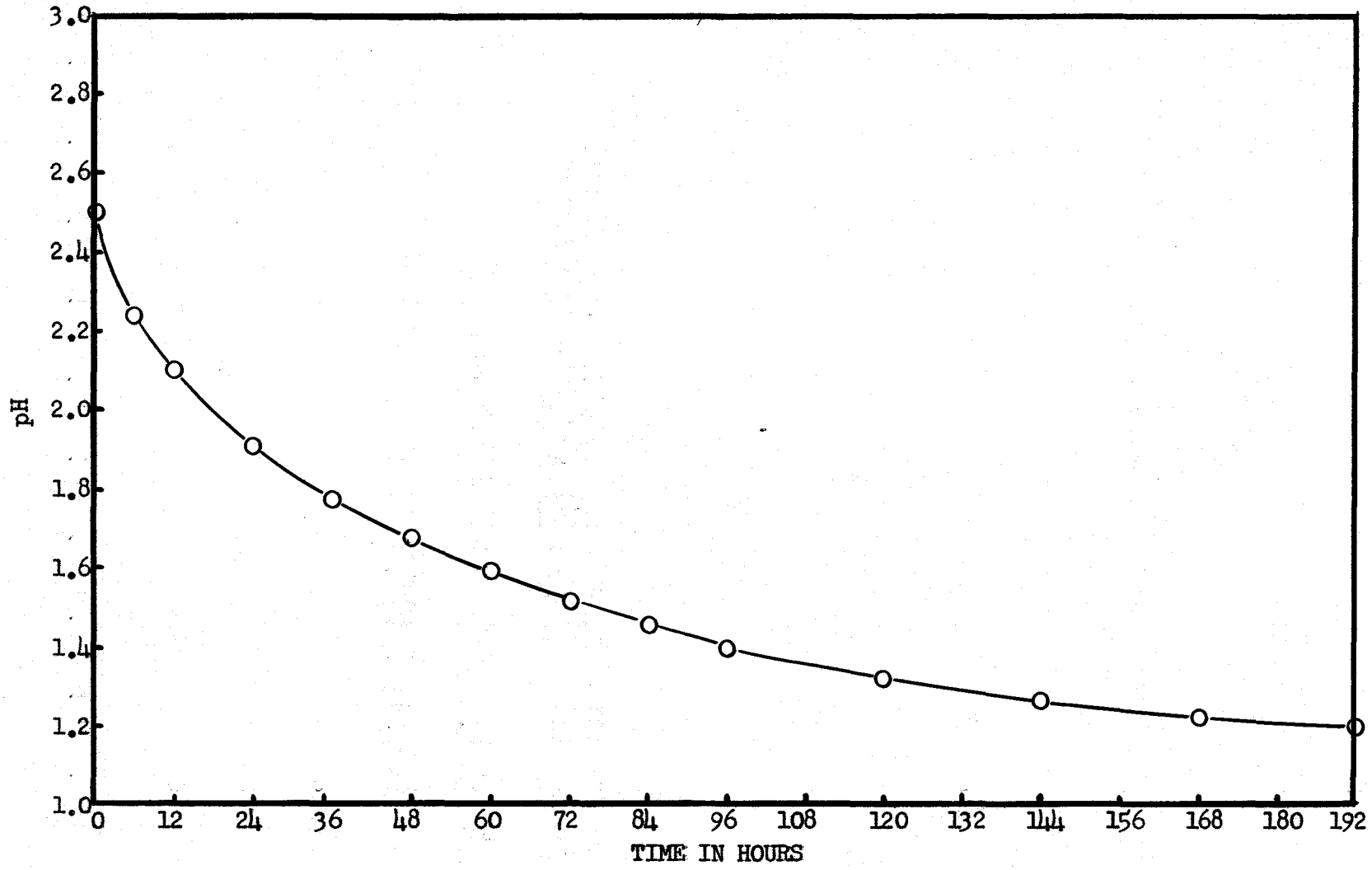

Fig. 19 The acidity produced by the biological oxidation of molybdenite concentrate mixed with pyrite.

nine months to determine the percentage of the molybdenum that was solublized.

The percolator that contained the molybdenite ore alone showed an oxidation of nearly thirty-six per cent while the percolator containing molybdenite ore mixed with the pyrite showed an oxidation per cent of fifty-five. Molybdenite was still being oxidized when this study was discontinued. The results of this investigation are listed in Table XXII.

TABLE XXII

PERCENTAGE OF MOLYBDENUM SOLUBLIZED FROM MOLYBDENITE ORE

Sample	Per Cent Solublized
Molybdenite Ore	35.9
Molybdenite Ore Mixed with Pyrite	55.0

The results indicate that a more efficient leaching of the molybdenum can be obtained when pyrite is mixed with the molybdenite ore.

R. The Influence of the Phosphate Ion Concentration on the Biological Oxidation of Molybdenite Concentrate

Since phosphorous is necessary for cell growth, an investigation was conducted to determine the optimum phosphate ion concentration needed for the biological oxidation of molybdenite.

A series of percolators were set up in the usual way and charged with 5 grams of molybdenite concentrate. The nutrient medium No. I was made up except that the phosphate (K_2HPO_4) was added in variable amounts as shown in Table XXIII.

Percolators in triplicate containing the same concentration of phosphate ion were inoculated with culture No. III and run in the usual manner. The soluble molybdenum at each concentration was determined weekly and recorded for a period of thirteen weeks. The results are given in Table XXIII and Figure 20. These results show an optimum phosphate ion concentration which is close to 50 parts per million. The

TABLE XXIII

THE INFLUENCE OF THE PHOSPHATE ION CONCENTRATION ON THE BIOLOGICAL OXIDATION OF MOLYBDENITE CONCENTRATE

Phosphate Ion Concentration Parts Per Million	Cumulative Soluble Mo (mg)
0	186.99
25	375.12
50	436.49
75	400.26
100	373.93
150	355.50

optimum phosphate ion concentration is not critical as shown by the gentle slope of the parameter in Figure 20.

S. <u>The Influence of the Phosphate Ion Concentration on the Biological Oxidation of Pyrite</u>

The effect of the phosphate ion concentration was extended to the biological oxidation of pyrite. The determination was performed in a similar way to the procedure described in topic R. These results are given in Table XXIV and Figure 21. The optimum is the same as that obtained in the preceding study which is 50 ppm. This study was run for

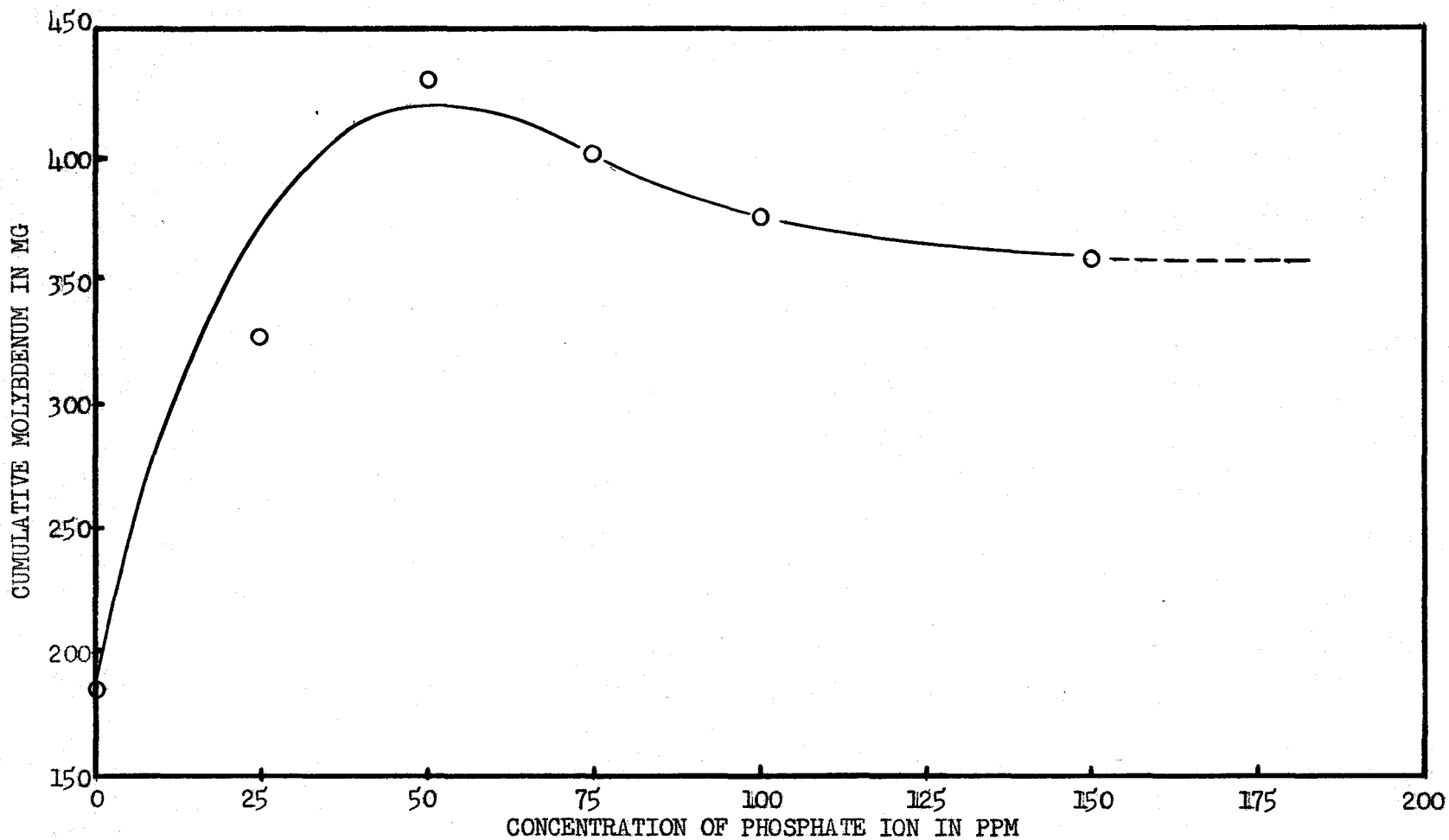

Fig. 20 The influence of phosphate ion on the molybdenite concentrate oxidation.

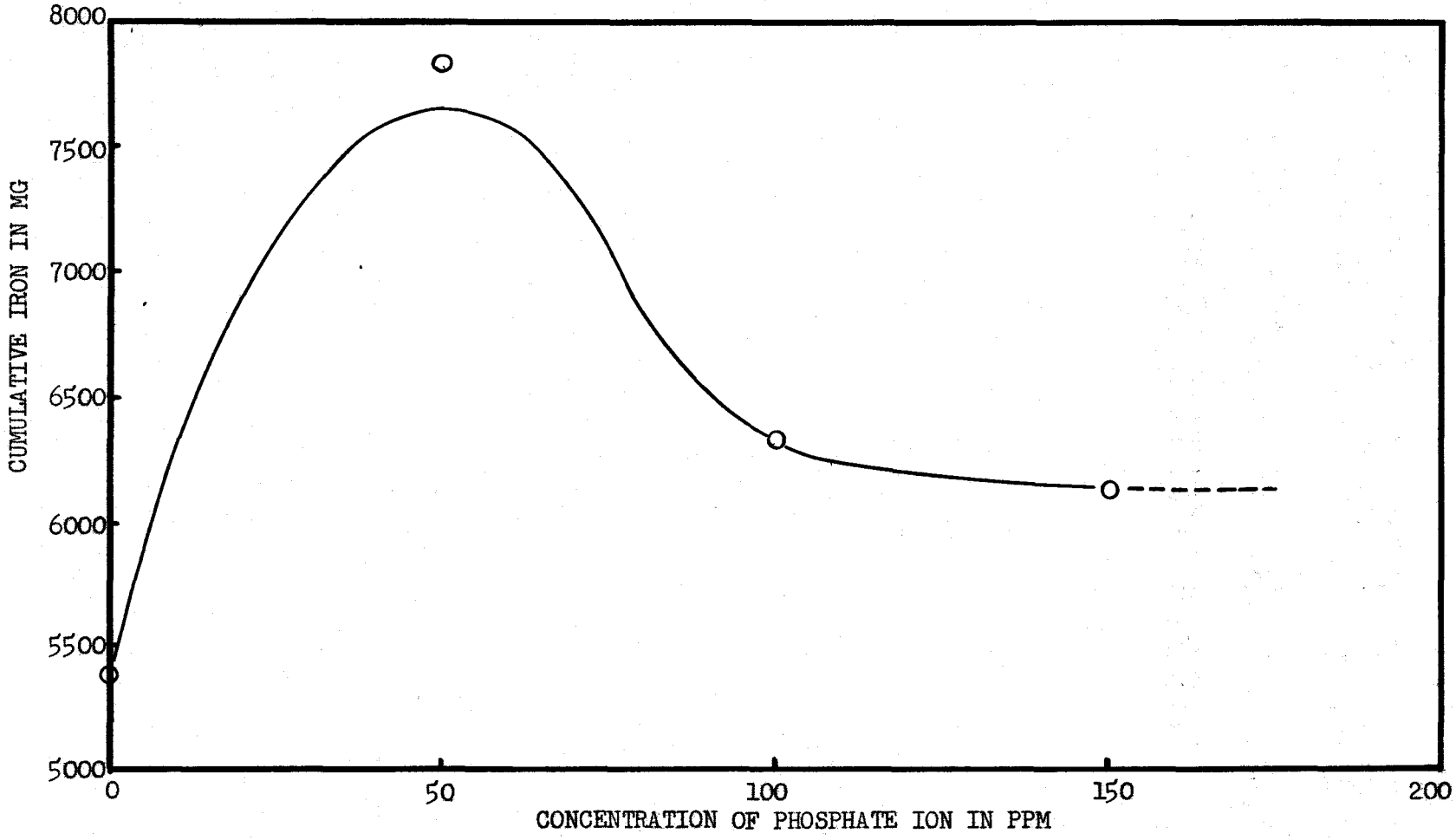

Fig. 21 The effect of the phosphate ion concentration on the pyrite oxidation.

twelve weeks.

TABLE XXIV

THE EFFECT OF THE PHOSPHATE ION CONCENTRATION ON THE PYRITE OXIDATIVE PROCESS

Phosphate Ion Concentration Parts Per Million	Cumulative Soluble Fe (mg)
0	5410.95
50	7738.1
100	6351.1
150	6183.9

T. The Effect of the Molybdate Ion on the Biological Oxidation of Pyrite

To determine the effect of the molybdate ion on the biological oxidation of pyrite, a series of percolators were charged in the usual manner and 5 grams of pyrite No. II was added. Different concentrations of the molybdate ion were added to nutrient No. II in the range of 0 to 500 ppm. Two percolators were chosen for each concentration and filled with the desired nutrient medium. These percolators were then inoculated with culture No. III. No bacterial activity was observed in the percolators with concentrations greater than 50 ppm. Because of this inhibitive effect, another series of percolators were set up to obtain high activity with the pyrite before the different concentrations of the molybdate ion were introduced. The molybdate ion concentration range used was from 0 to 60 ppm. This study was run for forty-two days. This proved successful and the results are tabulated in Table XXV and shown in Figure 22.

There seems to be no recognizable effect of the molybdate ion on the biological oxidation of pyrite in the range studied when the molybdate

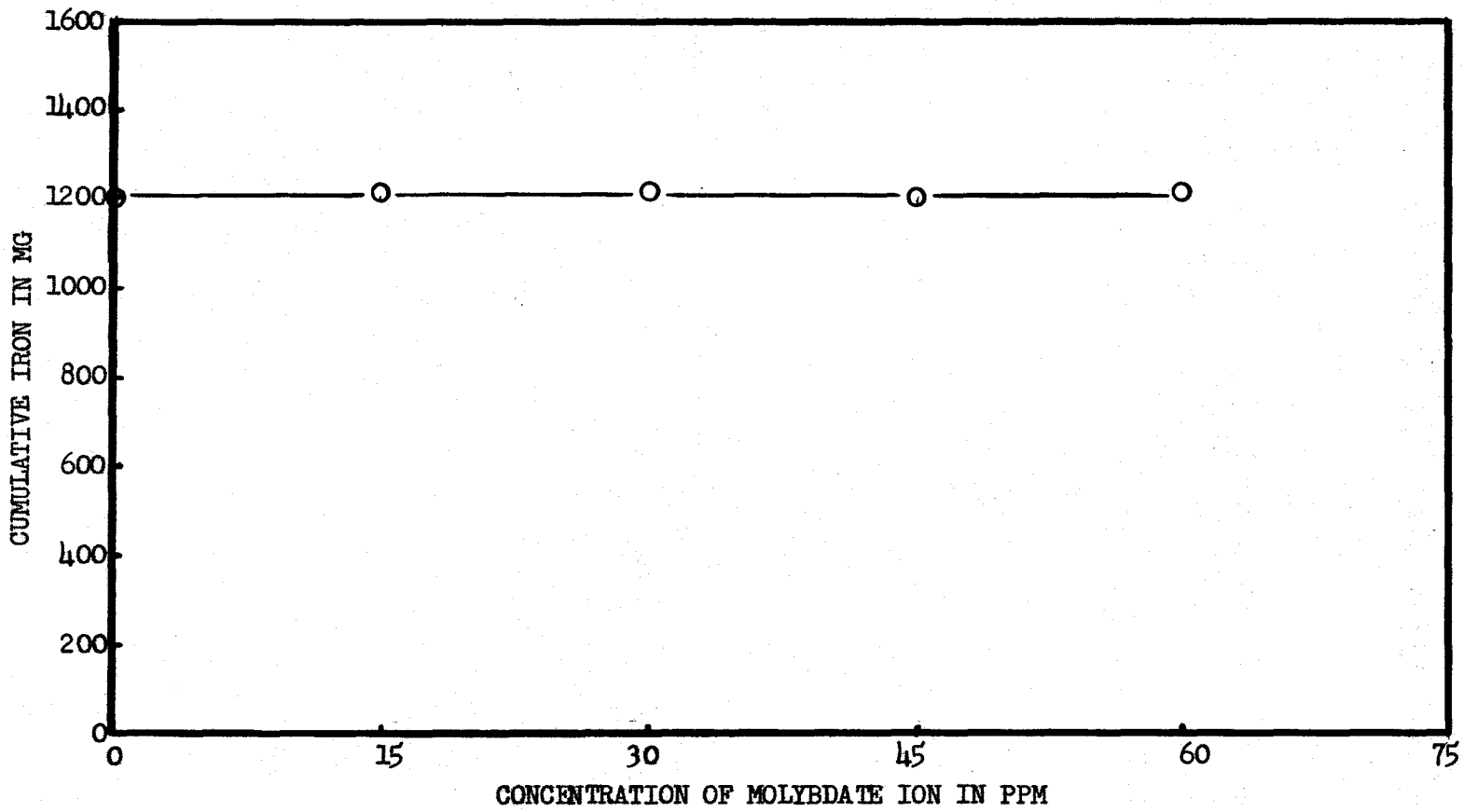

Fig. 22 The effect of the molybdate ion concentration on the biological oxidation of pyrite.

TABLE XXV

THE EFFECT OF THE MOLYBDATE ION ON THE BIOLOGICAL OXIDATION OF PYRITE

Concentration of $MoO_4^=$ ppm	Total Solublized Fe (mg)
0	1213
15	1218
30	1219
45	1198
60	1216

ion is mixed with the nutrient media after there is high activity in the percolators. There is a toxic effect when the concentration of the molybdate ion is greater than this.

U. The Effect of Aluminum Ion Concentration on the Biological Oxidation of Molybdenite Concentrate

The leaching streams in Bingham Canyon contain a high concentration of aluminum ion, so a study of the effect of the aluminum ion concentration on the biological oxidation of molybdenite was performed.

The nutrient No. I was modified by changing the phosphate ion concentration to that found in the optimum phosphate ion study and then a series of percolators having nutrient media of different Al^{+++} concentrations as shown in Table XXVI were charged and run under ordinary conditions for eighty-four days. The results of this study are tabulated in Table XXVI and represented graphically in Figure 23.

These results indicate there is an optimum concentration in the range of 325 ppm of aluminum ion. Concentrations greater than this

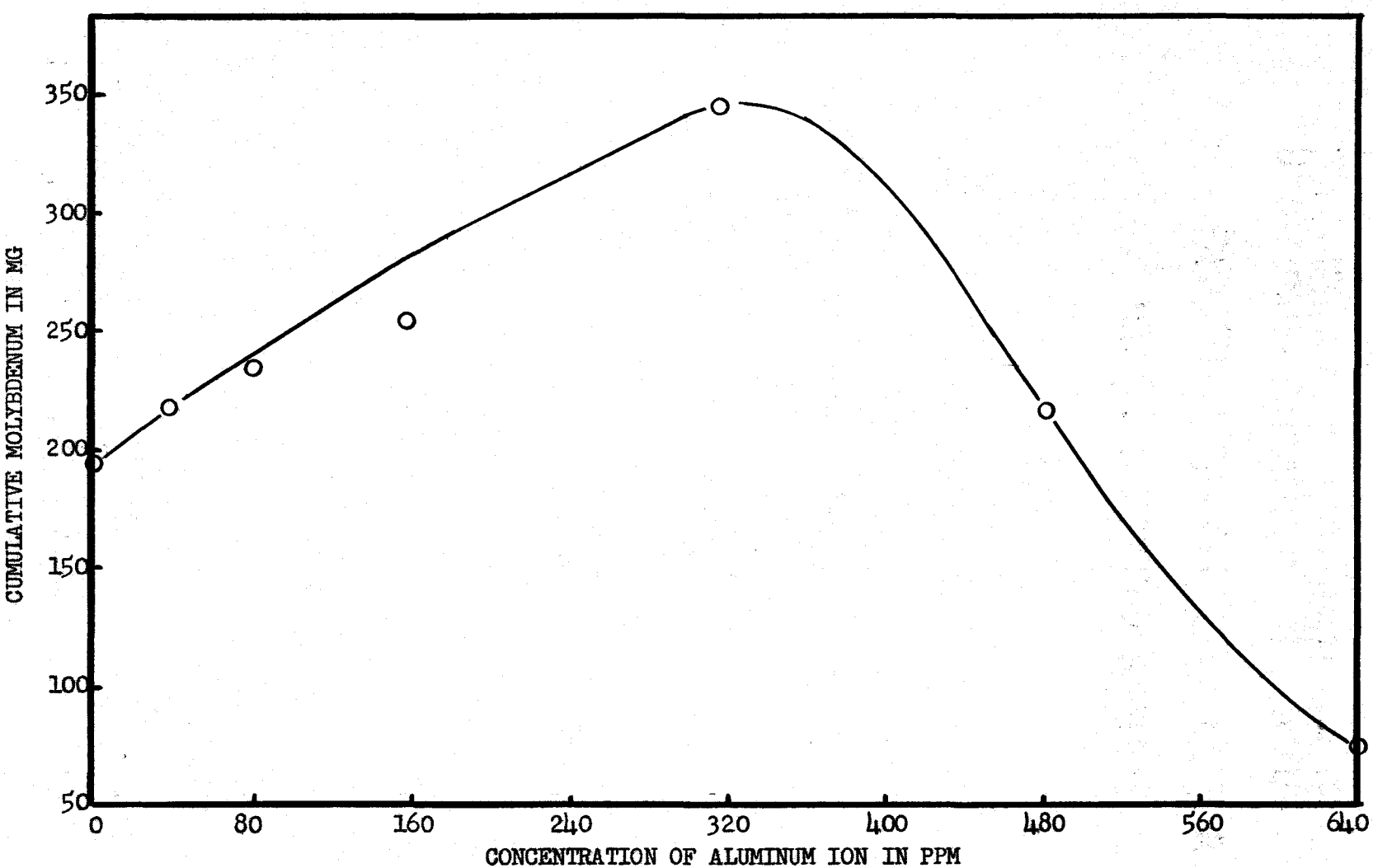

Fig. 23 The effect of the aluminum ion concentration on the biological oxidation of molybdenite concentrate.

decreased the rate of oxidation.

TABLE XXVI

THE EFFECT OF ALUMINUM ION CONCENTRATION ON THE BIOLOGICAL OXIDATION OF MOLYBDENITE CONCENTRATE

Al^{+++} Concentration (ppm)	Cumulative Mo in mg
0	187.58
40	219.20
80	225.31
160	248.96
320	345.13
480	217.16
640	66.59

CHAPTER V

SUMMARY AND CONCLUSIONS

The several investigations performed in this study provided conclusive evidence that molybdenite can be oxidized by the aid of soil microorganisms. Soluble molybdenum was readily formed in the percolators from molybdenite concentrate and molybdenite ore that were inoculated with Bingham Canyon stream microorganisms.

Samples of molybdenite concentrate that were inoculated with the Bingham Canyon stream bacteria increased the rate of production of soluble molybdenum by seven times that in the sterile sample, while samples of molybdenite concentrate that were mixed with pyrite and inoculated with the same culture increased the rate of production of soluble molybdenum twenty-nine times more than that formed in the control.

The samples of molybdenite concentrate mixed with chalcopyrite, molybdenite concentrate mixed with pyrite having a high copper content, and molybdenite ore having a considerable amount of copper sulfide all showed that the copper sulfide was oxidized first. When the leached copper concentration per week dropped to approximately forty parts per million, the molybdenite underwent significant oxidation. When various amounts of soluble copper were added to the percolators, no effect was detected upon the biological oxidation of molybdenite. Copper concentrations up to seventy-five parts per million were used. The reason for the preferential oxidation of the copper sulfide minerals over the molybdenite is not known. It may be due to the differences in the crystal

structures of the sulfide minerals. The copper sulfides may be slightly more soluble than the molybdenite which may favor the oxidation of the copper sulfide minerals over the molybdenite.

There were no components found in the Bingham Canyon streams that would precipitate the molybdate ion. If the molybdenite content of the low grade ores in Bingham Canyon is oxidized, it should be found in solution.

The amount of leaching is a function of the molybdenite ore particle size. A decrease in the diameter of four gave an oxidation increase of four hundred per cent.

The samples of molybdenite concentrate that were mixed with pyrite showed a three hundred fifty per cent increase over the molybdenite concentrate alone. When pyrite was mixed with molybdenite ore it increased the amount of solublized molybdenum forty-five per cent. A study of the effect of the ferrous iron concentration on biological oxidation of molybdenite concentrate showed that greater activity could be attained when ferrous iron was present.

Repeated bacterial transfers show a more efficient leaching.

The soluble molybdenum was found to be about one-fifth in the pentavalent and four-fifths in the hexavalent state. The reaction was assumed to be as follows:

$$2MoS_2 + 19/2\ O_2 + 8H^+ \longrightarrow Mo_2O_5 \cdot XH_2O + 4H_2SO_4$$

$$Mo_2O_5 \cdot XH_2O + 1/2\ O_2 \longrightarrow 2MoO_3 \cdot H_2O + (X-2)H_2O$$

The pH measurements showed an increase in the acidity.

The percentage of molybdenum solublized from the ore was found to be thirty-six per cent when the ore was oxidized alone while fifty-five per cent was solublized in the presence of pyrite.

The studies with varying phosphate concentrations showed an optimum concentration of approximately fifty parts per million for the biological oxidation of molybdenite and pyrite.

Different concentrations of molybdate ion showed that no bacterial activity was observed with initial inoculation to percolators containing the molybdate ion in concentrations greater than fifty parts per million. However, if high activity was attained in the pyrite media before the molybdate ion was introduced, no noticeable effect was found in concentrations up to sixty parts per million molybdate ion.

The effect of aluminum ion resulted in a modification of nutrient No. I. There appeared to be an optimum for the molybdenite oxidation which was approximately three hundred twenty-five parts per million of aluminum ion. Concentrations greater than this appeared to inhibit the oxidation somewhat.

These results provide conclusive evidence that molybdenite can be oxidized with the aid of soil microorganisms.

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OXIDATION OF MOLYBDENITE
WITH THE AID OF MICROORGANISMS

ABSTRACT OF THESIS

by

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MASTER OF SCIENCE

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ABSTRACT OF THESIS

OXIDATION OF MOLYBDENITE WITH THE AID OF MICROORGANISMS

This work represents a study on the biological oxidation of molybdenite, MoS_2. The principal objective of this study was to investigate the possibility of the biological oxidation of molybdenite, to determine the physical and chemical conditions under which the oxidative process occurs, and to develop a strain of bacteria or alter the activity of the microorganisms by acclimatization to increase their activity on sulfide minerals, in particular molybdenite.

Minerals used in this study were pyrite (FeS_2), chalcopyrite ($CuFeS_2$), molybdenite concentrate, and molybdenite ore.

The microorganisms used in this investigation were autotrophic bacteria obtained from the leaching streams of Bingham Canyon, Utah.

The apparatus consisted of sixty-four airlift percolators containing Ottawa sand (SiO_2) as a dispersing medium for the finely divided sulfide minerals.

The studies were performed by inoculating the solutions in the percolators with active cultures and comparing the amount of soluble molybdenum and other desired components produced with the amount found in a controlled sample.

The effect of the following ions in the nutrient requirements: phosphate, ferrous iron, cupric copper, and aluminum on the molybdenite oxidative process were studied. The result of mixing pyrite and chalcopyrite with molybdenite concentrate for oxidation was also

determined. The effect of the molybdate ion and phosphate ion concentrations were determined on the biological oxidation of pyrite.

Studies were performed on the biological oxidation of molybdenite ore and molybdenite ore mixed with pyrite to determine the percentage molybdenum solublized, also the relative oxidation states of the solublized molybdenum.

The effect of repeated bacterial transfer and molybdenite ore particle size was determined upon the biological oxidation.

There were no components found in the Bingham Canyon streams that would precipitate the molybdate ion.

Although these results were obtained from a synthetic media under laboratory conditions, they have provided conclusive evidence that it is possible to oxidize molybdenite by the aid of soil microorganisms.