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THE ELECTROLYTIC PURIFICATION OF AN IMPURE CADMIUM
SULFATE SOLUTION WITH A CELL UTILIZING A
MERCURY CATHODE AND A LEAD ANODE

by
W. D. McMaster

A Thesis

Submitted to the Department of Metallurgy
in Partial Fulfillment of the
Requirements for the Degree of
Bachelor of Science in Metallurgical Engineering

Montana School of Mines

Butte, Montana

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22732

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TABLE OF CONTENTS

Title	Page
Introduction -----	1
Problem -----	3
Preparation of Solution -----	4
Construction of the Cell -----	5
Operation of the Cell -----	8
Conclusions -----	13
Recommendations -----	14
Bibliography -----	17

THE ELECTROLYTIC PURIFICATION OF AN IMPURE CADMIUM
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INTRODUCTION:

Cadmium is produced solely as a by-product and all cadmium of commerce is obtained from zinc ores. It is a rare occurrence when zinc deposits are found which do not contain some cadmium.¹

One of the most important sources for the production of cadmium is the purification residue obtained from the zinc dust purification of zinc sulfate solutions. Zinc dust is added in the latter stages of the zinc leach cycle to remove impurities detrimental to the electrolytic deposition of zinc. The solution treated is the overflow from the neutral leach operation. If this neutral leach is properly carried out, iron, silica, alumina, arsenic and antimony will be precipitated before the zinc dust purification step. However, the overflow from the neutral leach will contain impurities such as copper, cadmium, and minor amounts of other impurities such as germanium, cobalt and nickel. The addition of zinc dust precipitates these impurities which are filtered out of solution. The

resulting purification residue is then treated to recover zinc, copper and cadmium.

This purification residue contains sufficient copper, zinc and cadmium to warrant further treatment for their recovery.² The cost of the subsequent cadmium extraction is thus borne largely by the zinc plant since treatment of the residue is necessary from the zinc-recovery standpoint.

The purification residue is leached with dilute sulphuric acid to remove as much of the zinc and cadmium as possible. The residue can either be leached in the oxidized or unoxidized condition. If the residue is oxidized previous to leaching, the speed of solution of zinc and cadmium will be increased; however, a greater proportion of copper and other impurities will be taken into solution. On the other hand, if the residue is leached in the unoxidized condition, hydrogen will be formed and, if arsenic is present, arsine gas will be formed. This gas is extremely toxic.³

The oxidized residue is usually leached by spent electrolyte until the acid is neutralized. When the residue is leached in this manner, most of the zinc and cadmium is leached and also a considerable portion

of the copper. The remaining residue containing copper and other insoluble material is settled out and is shipped to a copper smelter for treatment. The overflow is then treated with zinc dust to precipitate a very large proportion of the copper. This precipitate can either be added to the copper residue or can be sent back to the leaching division. The cadmium in the overflow is precipitated by further additions of zinc dust to obtain a cadmium-zinc sponge.⁴

The sponge, after oxidation, is leached to obtain the cell feed to be introduced into the electrolytic cadmium cells. This leach solution contains large amounts of cadmium and zinc in addition to very minor amounts of copper, cobalt, etc.

The high cost of producing zinc dust enhances the possibilities of removing impurities by other methods. It is with this thought in mind that this thesis is concerned. Although cadmium sponge was used, the application of the method of purification outlined in this thesis could be used to purify solutions in place of zinc dust purifications.

PROBLEM:

The purpose of this investigation is to determine the possibility of electrolytically purifying an

impure cadmium sulfate solution with the use of a cell containing a mercury cathode and an insoluble lead anode. The solution used was obtained by leaching impure cadmium sponge with diluted commercial sulphuric acid.

PREPARATION OF SOLUTION:

The material used to prepare the feed to the cell was an impure cadmium sponge and chemically pure sulphuric acid. The sponge was first pulverized and placed in a drying oven to drive off all moisture. The dried sponge was then passed through rolls and screened to remove all minus 20 mesh material. All plus 20 mesh material was passed through the rolls a second time and the undersize again screened off. This procedure was repeated until all material passed the minus 20 mesh screen size. The material was then mixed and placed in containers for subsequent use.

The leach solution was prepared by diluting commercial sulphuric acid with water to obtain a 25 per cent acid solution.

Winchester bottles placed on rolls were used for the agitation of the sponge and leach solution. A portion of the chemically pure acid was placed in

each Winchester Bottle. Sufficient cadmium sponge was added to produce a neutral solution. The pulp was then agitated for periods of three hours. After agitation the pulp was filtered through buckner filters. The filtrate thus obtained was found to be entirely free of copper. This necessitated the roasting of the sponge to produce oxidation. The roasted sponge was again leached and the pulp filtered to produce the desired solution containing an appreciable amount of zinc, cadmium, copper, and very minor amounts of other substances.

CONSTRUCTION OF THE CELL:

A glass beaker served as the container for the first cell constructed. Mercury was introduced into the beaker to serve as the cathode. Connection to the external circuit was made by introducing into the mercury a copper wire sealed in a glass tube. The tube served as an insulator between the copper wire leading to the mercury and the sulfate solution introduced in the beaker. A perforated lead plate was suspended in the solution parallel to the mercury surface. This lead plate served as the anode for the cell.

Direct current was supplied to the cell through the use of an alternating current rectifier. Voltage control was maintained by variable resistors placed in series. A milliammeter and a voltmeter were also placed in the circuit in order that desired voltages and current densities could be maintained.

Certain difficulties arose in the initial operation of the cell that necessitated a change of construction. The lead anode placed parallel to the mercury surface quickly became polarized by the adsorption of gases to its surface. Also, the connection between the anode and external circuit was found to corrode rapidly. The cause of this was the ability of the copper wire to serve as a soluble anode and enter the solution. A third difficulty was the large volume of solution contained within the beaker. In order to save time in electrolysis it was realized that a smaller cell should be built.

A second cell was constructed to eliminate the difficulties that became apparent in the operation of the first cell. The container for the second cell consisted of a test tube. The connection between the mercury cathode and the external circuit was made by sealing a platinum wire into the bottom of the tube.

The lead anode was shaped to a point and introduced into the cell. The tapered anode allowed the escape of gases and thus prevented polarization due to adsorbed gases. This anode was also made of such length that, when introduced into the sulfate solution, the anode would project above the surface of the solution. This offset the corrosion of the submerged connection used in the first cell. The small volume of the test tube limited the volume of solution introduced to a point where electrolysis would not have to proceed for undue lengths of time.

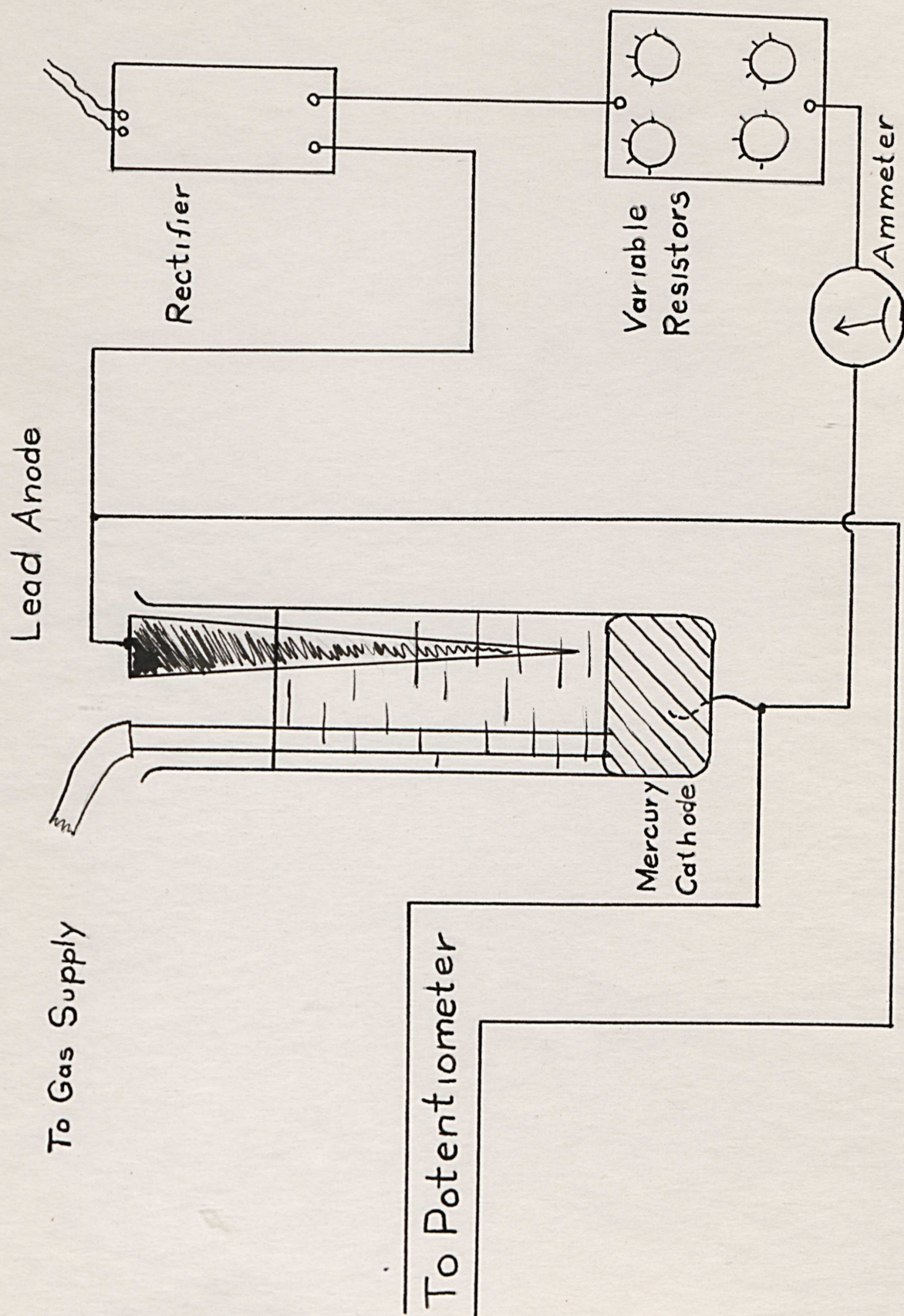
The cell was first operated in order that a plot of current against voltage could be obtained. It was found in the initial operation that readings taken from the voltmeter were too insensitive and also quite inaccurate. This necessitated replacing the voltmeter with a potentiometer in order that more precise readings could be obtained. The potentiometer was standardized against a standard Weston cell. The potentiometer proved to be satisfactory for the purpose indicated; however, before readings could be taken that would be reproducible, a method had to be devised to promote amalgamation between the mercury and deposited metals. To promote amalgamation a glass

tube connected to a natural gas supply was introduced into the cell. The tip of the tube was placed just beneath the mercury surface to assure agitation of the surface when the gas was applied. Natural gas was used instead of compressed air to insure the continued reduction of the electrolytically deposited metals. The introduction of gas under pressure was found to be sufficient to promote amalgamation and maintain a fresh cathode surface. Cell construction is shown on page 9.

OPERATION OF CELL:

Voltage and current readings were taken with small increases in current. These readings are tabulated on page 10 and are shown graphically with voltage as abscissa and current as ordinate.

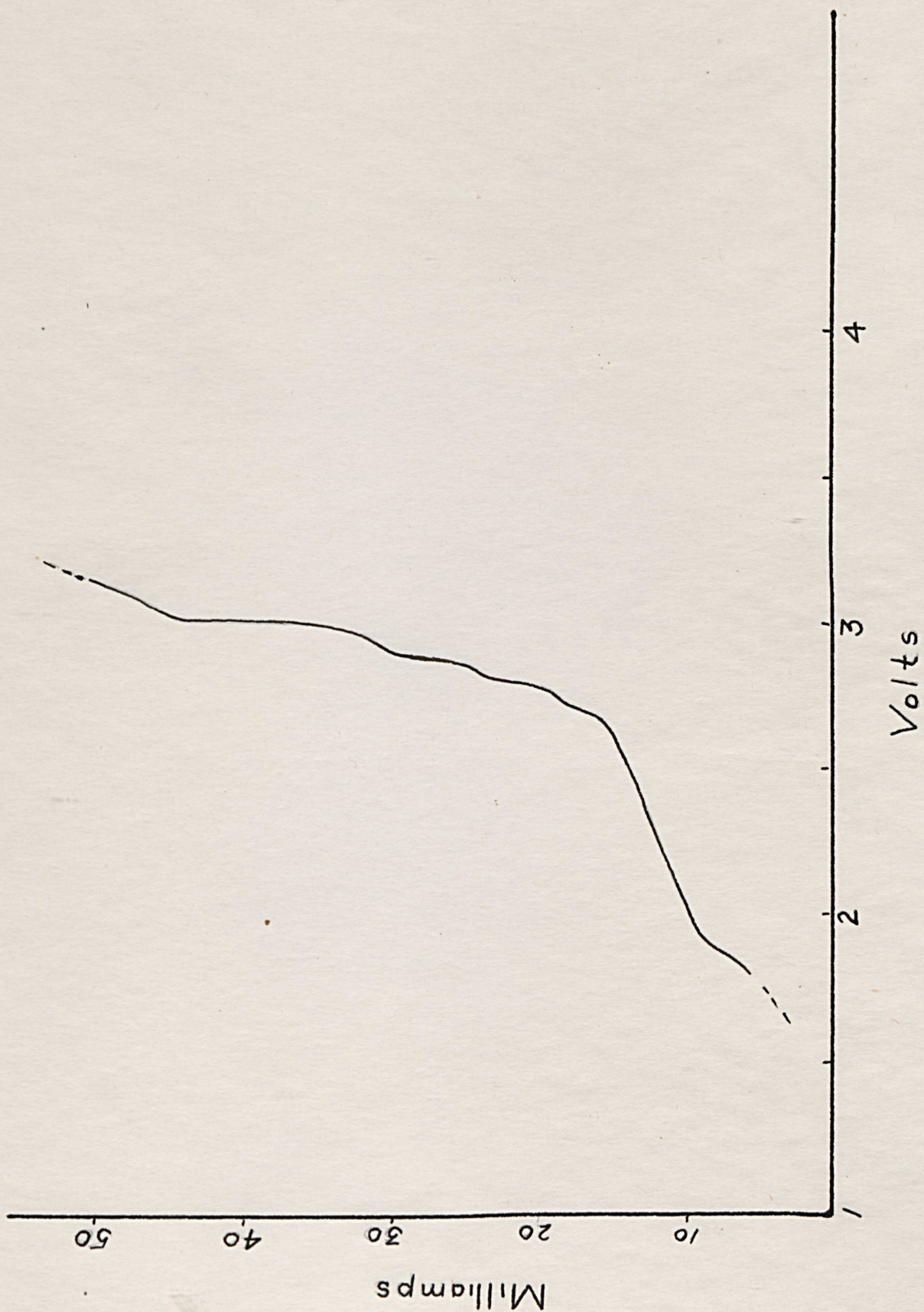
Definite variations in the continuity of the plot can be observed corresponding to the decomposition potential of the various ions present. Since decomposition voltages of various metals and their anions vary somewhat with concentration and types of electrodes used, no definite values can be assigned to the elements in the solution. The decomposition voltages are, however, in definite relation to each other.



Cell and Circuit

Potentiometer and Milliammeter Readings

<u>Volts</u>	<u>Milliamperes</u>
1.864	7
1.879	8
1.918	9
1.965	10
2.624	12
2.666	15
2.710	16
2.742	18
2.791	20
2.822	23
2.859	25
2.887	27
2.926	30
2.973	32
2.993	35
3.018	37
3.045	40
3.059	42
3.070	45
3.100	47
3.104	50



Creighton and Loehler have tabulated decomposition potentials for different electrolytes of molal concentration between platinum electrodes.⁵ Some of these values are given below.

<u>Electrolyte</u>	<u>Decomposition Voltage (volts)</u>
Zinc sulfate	2.55
Cadmium sulfate	2.03
Cobalt sulfate	1.92
Copper sulfate	1.49

It is apparent that quite a difference exists between the decomposition voltages of the metals and sulfates with which we are concerned. It should be possible then to eliminate stepwise each metal present.

According to Creighton and Koehler this has been investigated by Freudenberg.⁶ By employing graded electromotive forces he succeeded in effecting separations between metal ions in acid solution. On this premise, then, I have operated my cell in such a way as to apply an electromotive force sufficient to eliminate copper from solution.

The cell was first operated at a voltage of 2.7 volts and a current of 20 milliamps. This corresponded to the second variation in the voltage-current curve. It was assumed that this corresponded to the decom-

position potential of cobalt. Cobalt being higher than copper, both should be deposited leaving a cadmium zinc solution.

Fresh solution was introduced into the cell and the current applied. Since the copper ion is blue this characteristic was used as a control on the length of electrolysis. The solution was electrolyzed for six hours, the time required for the complete removal of copper. The remaining solution was then filtered and analyzed qualitatively. It was found that only zinc, cadmium and a minor amount of cobalt remained. The qualitative procedure followed has been outlined by Evans, Garrett, and Quill in their manual Semimicro Qualitative Analysis.⁷ The reduced elements were found to be almost entirely amalgamated with the mercury.

CONCLUSIONS:

The desired separation of impurities other than zinc and cobalt was accomplished with successful amalgamation of the reduced impurities. The presence of zinc in the cadmium electrolytic circuit is not detrimental as the return electrolyte can contain zinc up to a point where cadmium is in excess of zinc

22732

by 10 to 15 grams per liter. It should be possible to eliminate the cobalt from the solution either by prolonged electrolysis or by the application of a greater electromotive force.

The mercury cathode possesses qualities that are desirable in work of this nature. The hydrogen overvoltage of mercury and its amalgams is very high.⁸ Thus, strong current densities can be applied without liberation of hydrogen. The fluidity of the mercury is to be desired for the ease with which it can be extracted from and introduced into the cell. One disadvantage of using mercury is the poisonous nature of the mercury vapor formed upon distillation. However, with the proper apparatus the mercury could be distilled with ease and very little danger.

The possibility exists that this method of electrolysis can be applied in other processes where the decomposition potential of the ions is great enough to permit a quantitative separation.

RECOMMENDATION:

The object of this problem was to establish the possibilities of using this type of cell in the purification of cadmium sulfate solution. The

procedure, therefore, was conducted only in a qualitative way. In the event further research is done on this thesis, I would recommend the following suggestions be followed.

1. A complete qualitative and quantitative analysis be made on the solution prior to introduction into the cell.

2. A pure mercury cathode be used at the start of each electrolysis.

3. A number of aliquots of solution be electrolyzed, varying the current density and time of electrolysis for various aliquots.

4. After each electrolysis the mercury cathode be distilled and the residue analyzed.

5. A quantitative analysis be made on the electrolyzed solution for each aliquot. The analysis of both cathode and solution would serve as a check.

6. A close control and recording of voltage and current be maintained in order that power consumption and efficiencies can be calculated.

A procedure of this type would furnish detailed information on the progress of the electrolysis. It would also establish the possibility of removing each ion present both individually and economically.

The procedure as outlined on the preceding page would require a considerable amount of time and detailed work. It is suggested, therefore, that if further research on this thesis is contemplated, the work should be shared by two or possibly three individuals. The work could then be divided into phases with each individual performing work in one phase of the operation, much time could be saved and the accuracy of the results would be enhanced.

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