RECOVERY OF DIAMOND FROM POLISHING SLUDGE

GENERATED IN FINISHING OF CEMENTED

TUNGSTEN CARBIDE BALLS

By

VIVEK KUMAR DUBEY

Bachelor of Science

Mechanical Engineering

Visvesvaraya Regional College of Engineering

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Thesis Approved:

R. Koomanduri
Thesis Advisor

C. E. Price

R. Ramakrishan

Don A. Lucca

Thomas C. Collins
Dean of the Graduate College

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Dedicated to

My Grandmother
Smt. Sarala Mishra;
My Father
Shri Mahesh Kumar Dubey;
and
My mother
Smt. Priti Dubey
My MS is their 'Materialised Sacrifice'

SUMMARY

This project deals with the recovery of diamond from polishing sludge generated during the finishing of cemented tungsten carbide balls. Because of the extreme hardness (8000 kg/mm^2), very high wear resistance, and chemical inertness, diamond abrasives used in polishing do not degenerate significantly and hence can be recovered from the polishing sludge. Due to the high cost and strategic importance of diamond, recovery was practiced in the past and many techniques were developed for its recovery from various ores and swarfs containing materials, such as cement, cemented tungsten carbide, silica, glass, metals, and organic compounds.

The successful synthesis of diamond in the presence of a catalyst-solvent, in the mid 50's by researchers from General Electric, under high-pressure (~50 kbar)-high-temperature (~1500°C) [HP-HT] conditions, provided an alternate and dependable source of diamond. Since then, several tons of diamond was produced in the U. S and in other countries around the world. Consequently, diamond is no longer considered as a strategic material as its supplies are plentiful domestically. Many large industries which used to recover diamond mainly because of its geographic importance discontinued the practice of diamond recovery. Further, the economics, the complexity in collecting and sorting out, and storage of different sludges generated during grinding/polishing of different materials, seemed to justify the approach in these cases.

Small industries in the U.S, involved in polishing advanced materials and using diamond abrasives are increasingly finding keen competition in companies from the developing countries, where the wages are significantly lower. Any savings in consumable costs (diamond abrasives) in those cases can often make or break their competitive

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advantage. It is with these companies in mind that this project was undertaken. Moreover, Occupational Safety and Health Association (OSHA) regulations and growing environmental concerns require that such sludges be disposed off deligently. Hence, from an economic as well as environmental stand point, the techniques of recovery of diamond from polishing sludge need to be such that the least amount of chemicals be employed.

Polishing sludge containing tungsten carbide and diamond particles was obtained from an industry in batches of 20 liters. As there is considerable difference in densities of the constituents, a centrifuging method was employed to separate them. However, centrifuging resulted in a dense mass which became extremely hard after removal of oil by heat and was difficult to crush. The process was therefore discontinued and attempts were made to separate diamonds by using a high density liquid, such as methyl iodide. However, methyl iodide is expensive for this application and its fumes are toxic. Hence, the technique was discontinued. Skin flotation using inorganic surfactants was then attempted. However, its yield was rather low (0.1% by weight of powdered sludge). Hence, this method was not considered attractive as an industrial process. Chemical methods resulted in 20% yield by weight of sludge treated, but the material contained significant amounts of dark carbonaceous material in addition to diamond. Due to the caustic nature of the chemicals involved, as well as economic, and environmental considerations, chemical methods were discontinued. For example, about $30 was spent per 100 gram of sludge treated, by way of chemicals and processing alone.

The technique developed in this investigation explores the technical feasibility of an environmentally safe method of diamond recovery. We have developed a laboratory method that has resulted not only in high yield of diamond powder (19% by weight of powdered sludge and ~90% of the diamond present in 100 grams of powdered sludge) but also in the recovery of oil used in the polishing operation. The high yield of diamond justifies the development of a prototype system for recovering diamond from large quantities of polishing sludge. In applications where large volumes of diamond powder is

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used per year (quarter million dollars or about 25 kg of diamond abrasive) for polishing one specific material (in the present case, cemented tungsten carbide), the simple technique we have developed appears to be technologically viable.

Dedicated to

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CHAPTER 1

INTRODUCTION

Finishing operations such as grinding, lapping, and polishing are a necessity in the manufacture of components requiring good surface quality. Improved surface finish is a requirement not only for enhancing the life of components but also for the reliability of the component system as a whole, since surface flaws can cause fatigue failure of the components in service. For example, in the case of ceramic ball bearings, which are used for aerospace bearings, high surface finish (with average roughness [R_a] within a few nanometers) along with good sphericity (~50 nanometers) are important requirements for a long service life and reliability in service.

The ever increasing use of difficult-to-machine materials for improved performance demands harder tool materials and the improved finish of such tools becomes a natural consequence. Although abrasives such as, alumina, cerium oxide, magnesium oxide are finding increasing applications, diamond as an industrial grinding and polishing abrasive still remains indispensable. This is because of the unique properties of diamond including low friction (~0.01 in air), absence of adhesion between tool and most work materials, higher hardness and high wear resistance (and consequently less variation in size of the abrasive particles). This has resulted in a steady increase in the demand for the diamond powder. For example, the estimate of the demand for diamond was about 6, 737, 000 carats (including 750, 000 carats of reclaimed diamond powder), in 1950, and 9, 000, 000 carats (including 900, 000 carats of reclaimed diamond powder) in 1952. The recovered diamond powder has steadily grown to 2, 000,000 carats in 1964 [1], after which it has

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precipitously dropped to almost negligible amount due to the reasons outlined earlier. Assuming that the reclaimed diamond forms 10% of the diamond powder in use, the demand for diamond powder was about 20, 000, 000 carats in 1964. Assuming that the demand for diamond has grown linearly over the years, and projecting these figures to 1990, the demand may be calculated to be about 45, 000, 000 carats.

Inspite of the successful synthesis, diamond is still rather expensive ($1 to 1.5 /carat) due to the HP-HT technologies and can be beyond the reach of many industries under the intense competition. Reuse of reclaimed diamond can be a viable alternative for such industries to minimize their consumable costs. The ever increasing concern for the environment, the high cost of disposal of industrial wastes (upto $1500/barrel), and the legalities associated with these are gaining importance. It, therefore, becomes even more important to consider the reuse of important resources. Materials such as diamond, tungsten, and cobalt are not only non-biodegradable but also expensive. This becomes an important consideration for the disposal problem and an opportunity for their economic recovery. Oil recovery was considered here from purely ecological reasons although the emphasis of this project is on diamond recovery. Well established methods are available for the separation of cobalt and tungsten carbide. Hence, this task was not undertaken in the present investigation.

Since, diamond has high wear resistance, it does not degrade appreciably when lapping over a short duration of time (2 to 3 hours). But, when carried out for long periods (100 to 200 hours), as in the case of polishing cemented tungsten carbide pen balls, size reduction of diamond takes place.

As pointed out earlier, recovery of diamond from ores and from various industrial wastes is not a new problem and several techniques using mechanical, electrical, chemical, electrostatic, and electro-chemical principles have been applied with considerable success. However, some of these methods may not be acceptable in our society (in particular caustic chemicals), due to the high costs and the difficulty involved in their disposal. Magnetic

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methods can be cumbersome for recovering very small particles ($< 2 \mu m$). Consequently, the thrust of the project has been on developing a simple physical method for the recovery of diamond from the polishing sludge with minimal use of chemicals in general and no caustic chemicals in particular.

A technique has been developed for the physical separation of diamond from the polishing sludge generated in the finishing of cemented tungsten carbide pen balls. The sludge consists of a mixture of tungsten carbide, cobalt, lapping oil and diamond particles. This sludge is currently considered as a waste generated during the polishing process and is disposed off by some industries without diamond recovery. The cost of diamond abrasives used per year in some polishing industries can be rather significant ($250,000/year). Recovery of diamond from the polishing sludge can therefore result in significant savings in the polishing costs.

The outline of the thesis is as follows. In Chapter 2, a brief literature review of the various techniques for the recovery of diamond from cemented tungsten carbide sludge is given. Methods for the extraction of diamond from diamondiferous ores and for the recovery of diamond powder from different sources, such as the sludge produced in grinding of cemented tungsten carbide tool inserts and in mixtures of silica, cement, organic and other materials with diamond have been given in the Appendix I for completeness.

Chapter 3 defines the problem and outlines the scope of the work.

Chapter 4 gives details of the different methods used in this investigation for the recovery of diamond. This chapter is divided into two sections. The first section gives details of some of the chemical processes and the second section described by the physical method developed for the recovery of diamond from the polishing sludge without the use of chemicals. The recovery of diamond is first considered followed by that of the oil. Details of the process, including the flow charts of the process and the apparatus used are given. Critical experiments and important effects observed are also described.

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Chapter 5 is a discussion on the process developed, followed by Chapter 6 which deals with conclusions. Work in progress is given in chapter 7.

CHAPTER 2

LITERATURE REVIEW

Introduction

The methods employed for the recovery of diamonds can be classified under two headings: from minerals (extraction from diamondiferous ores) and separation from polishing /grinding sludges or swarfs and other impurities. Literature on both these topics has been reviewed and presented in Appendix I for completeness as well as its usefulness in general for diamond recovery. Separation of diamond from cemented tungsten carbide sludge is of immediate relevance to this investigation. Hence, the literature review covered in the following focuses on this aspect.

While methods used for the extraction of diamonds from minerals and ores generally deal with larger gem quality stones, usually measured in carats (1 carat=0.2 grams) and industrial diamond, those that handle polishing sludges deal with much finer size fraction of diamond (a few micrometers). Consequently, the methods employed in the former case differ from those in the latter case because of the size as well as the scale of operation. Nevertheless, they reveal useful insights that can be gainfully employed in the separation of diamond from the polishing sludge.

In this chapter, relevant methods for the recovery of diamond such as heavy media separation, electrolytic separation, skin flotation, and chemical methods have been reviewed. These may serve as a good starting point for the recovery of diamond from the cemented tungsten carbide polishing sludge. Hence, along with the Appendix I, these methods add to the generality of the report. The review is intended to facilitate the

understanding of the nature of the sludge and its response to different methods of separation, thereby giving direction to the work undertaken and in defining the problem.

Methods of Separation

Over the years, different methods for the separation of diamond from various ores and contaminants have been developed. The following is a list of some of the methods used industrially [1].

1. Centrifuging
2. Gravity Concentration
3. Grease Table Separation
4. Heavy Media Separation
5. Electrostatic Separation
6. Electrolytic Separation
7. Skin Flotation
8. Magnetic Separation
9. Chemical Separation.

Details on these techniques are given in Appendix I. Of the methods mentioned above, the first three methods are predominantly used in mines. The others deal with the recovery of diamond from various types of sludges. In the following, a brief description of some of the methods pertinent to the problem is given.

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Recovery of Diamond from Scrap Cemented Tungsten Carbide

Methods of Recovery of Diamond from Scrap Tungsten Carbide [2]

Following methods were developed for the recovery of diamond from scrap tungsten carbide:

1. Acid dissolution of cobalt binder, followed by that of cemented carbide

2. Oxidation under heat followed by alkali treatment

3. Fusion methods

4. Electrolysis

5. Skin flotation

It can be seen that except for the skin flotation method, all are chemical methods for the recovery of diamonds. These methods will be briefly discussed in the following.

1. Acid dissolution of Cobalt Binder Followed by Acid Dissolution of Cemented Carbide [2]: Material to be treated is first pulverized and then dissolved in a dilute nitric acid. This method is generally not considered for diamond recovery when the mixture contains large size particles. The depth of penetration of the nitric acid is limited and requires the maximum particle size to be less than 100 mesh. The reaction with fine powder is very vigorous and associated with the release of nitric oxide. This treatment removes cobalt.

Tungsten carbide, being chemically passive, is difficult to attack with normal acids, and hence requires the use of strong acids. Diamond swarf is placed in a platinum crucible and dissolved in a concentrated nitric acid with 10% by volume of 48% hydrofluoric acid. The mixture is alternately warmed and cooled (cooling it when the reaction becomes too vigorous). When further heating does not produce a marked reaction, a 10% hydrofluoric acid is added to dissolve all the material into solution. The solution is decanted and washed. This method is not suitable for industrial purposes as it is a costly process.

Although the recovery is ~99%, tungsten carbide and cobalt are dissolved and not removed in this case.

2. <u>Oxidation Under Heat Followed by Alkali Treatment</u> [2]: This method is used when fragments of cemented carbide and diamond are of size larger than 16 mesh. The yield is roughly 97.7%. When Diamond is of much smaller size (100 to 200) the yield reduces to between 50 to 85%. The large sized fragments are spread on a porcelain dish (or silica dish) and heated overnight for 12 hours in a furnace at 800 °C (or heat at 950 °C for 90 minutes.). They are then transferred to an iron pot and covered with 1.5 times its weight of sodium hydroxide. The pot is heated to bring sodium hydroxide to a molten state and then stirred intermittently while maintaining the mixture in a molten state for about 30 minutes. After cooling, it is mixed with water to dissolve soluble tungstates. The solution and the residue are transferred to a beaker. Supernatant liquid is decanted and the residue is washed a few times with water. The washed residue is warmed with 50-50 hydrochloric acid and nitric acid solution. The supernatant liquid (soluble cobalt) is decanted and diamond is separated.

3. <u>Fusion Methods</u> [2]: Most satisfactory results are obtained with a fusion mixture of 30 parts of sodium hydroxide and 2 parts of sodium nitrate added to 3 parts of powder with occasional additions of 1 part of sodium nitrate.

In one case, about 112 grams of cemented tungsten carbide (containing 15% of cobalt and 14 to 28 mesh size diamond powder) are treated with a fusion mixture of 500 grams of sodium hydroxide and 25 grams of sodium nitrate, taken in an iron pot, with additions of 5 grams of sodium nitrate every hour. Fusion is carried out for ~5 hours with intermittent stirring.The melt is then cooled and soluble tungstates dissolved in boiling water. After decanting the liquid, the residue is transferred to a beaker and boiled with hydrochloric acid. The portion of residue not attacked is transferred to an iron pot and fusion carried out for ~4 hours (using the same proportion of fusion mixture). The residue is washed after cooling and acid treated as earlier. Finally, the powder is dried after several

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washes with water and decanted/centrifuged. The recovery can reach approximately 97%. For fine sized powder (less than 60 mesh), the powder is added to a molten sodium hydroxide-sodium nitrate mixture (10 parts of fusion mixture to 1 part of powder), with intermittent stirring and additions of sodium nitrate (one part) every hour. The mixture is kept molten for 4 to 5 hours. After adding water and the mixture boiled, it is then transferred to a beaker and washed by decantation/centrifuging. A 50-50 mixture of hydrochloric acid and nitric acid is then added to the powder, and the mixture boiled and washed by decantation /centrifuging. The powder is then dried and analyzed for impurities. Fusion and cleaning processes are repeated if the powder still has considerable impurities.

As industry is rather concerned regarding the use of chemicals in general and caustic chemicals in particular for environmental reasons, this method was not pursued in the present investigation as a physical method was favored. Also, in this method cobalt and tungsten carbide are not recovered.

4. Electrolysis [2-4]: Electrolysis is carried out in an acid bath where tungstic acid is directly formed and cobalt is precipitated. Alternately, when sodium hydroxide bath is used, tungsten enters into solution as sodium tungstate and cobalt is precipitated out as black amorphous cobaltic hydroxide.

Tungsten Matrices [3-4]: Tungsten is a primary constituent of 'hard' matrices. Other materials present include other metals and alloys, such as nickel, vanadium, titanium, ferro-molybdenum and ferro-vanadium. Usually metallic binders such as cobalt, zinc, copper, nickel, tin, and iron are used. Since tungsten is not an active element, it is not attacked by acids easily. A mixture of 10% nitric acid and 5% mercurious nitrate was found to decompose such a matrix in ~2 hours at 8 A.

Other types of reducing agents (instead of mercurious chloride) when used with nitric acid, were found to give the following results :

i) 15% nitric acid with 5% glucose at 15 A (time: ~80 minutes.)

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ii) 20% nitric acid with 5% formaldehyde at 15 A (time: ~55 minutes)

iii) 15% nitric acid with 5% sodium potassium tartrate at 15 A (time: ~100 minutes).

Tungsten Carbide Matrices [3]: An electrolyte having 20% nitric acid, 2% hydrofluoric acid, and 5% sodium potassium tartrate was found to be quite successful. This was found to be suitable for a matrix with tungsten carbide : ferromolybdenum : nickle :: 15 : 5 : 1, binder has 58% copper and 42% zinc and has 3 parts of matrix to 1 part of binder. The process was found to take about 1.25 hours at 20 A. Under more severe situations 30% to 40% nitric acid + 2% hydrofluoric acid with potassium tartrate may be used at 20 A. It is found to take about 2.5 hours for decomposition of a tungsten matrix having iron as binder.

In electrolysis, chemical resistance and electrical conductivity are important considerations. When the electrolyte consists of nitric acid and hydrochloric acid and no nitrates are present, copper electrodes are found to be the most satisfactory. When the electrolyte consists of nitric acid, and hyrofluoboric or hydrofluoric acid, stainless steel electrodes (cathodes) are more suitable. In addition to the fact that this technique uses chemicals, tungsten carbide and cobalt are not recovered.

Other techniques that are used include magnetic separation followed by acid treatment or alkaline fusion, treatment with aqua regia, and fusion with potassium hydroxide for removal of tungsten carbide, cobalt and other metals. Once the organic contaminants, metals and carbides are removed, the skin flotation method is used to float diamond. Details of the skin flotation method are given in the following section.

5. Skin Flotation [3-5, and 7]: This method is suitable for segregating particle sizes between 10 to 20 mesh. Before flotation is actually carried out, the surface of diamond is cleaned of grease or adhering oxide coating. For this, processes such as ball milling are used. The diamond surfaces are then cleaned in an alkaline medium. Boiling in a solution of sodium hydroxide is preferred. Diamond then needs to be conditioned. Ammoniacal soap solutions of oleic acid, recinoleic and linoleic acids are found satisfactory.

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Once diamond is conditioned, it is taken in a beaker and a sufficient quantity of water is added to cover the diamond. The beaker is then tilted at an angle of 40 to 60 degrees and gently rotated. When sufficient number of diamond particles float on the surface of water they are decanted. The procedure is repeated until no more diamonds float. This method has been used successfully in the separation of diamonds from tungsten and cobalt. Improved methods report up to 98% recovery.

Skin flotation method is suitable because it uses chemicals only as surfactants. It assumes that the sludge is free of metals and other impurities that may also float along with diamond. It may be employed when diamond is fine and the contaminants are large.

In a variation of this method, the diamond polishing swarf concentrate is placed in a pyrex beaker, boiled in hydrochloric acid, and then diluted with about three times its volume of water. Carefully decanting and stirring causes the diamond particles to rise to the top and form a 'raft' on the top of the liquid held by surface tension forces. Diamond particles may be skimmed from the surface by decantation. This assumes, however, that the swarf of the ball material is dissolved by the acids.

In addition to the above methods, the following two methods were considered suitable for concentration and separation of diamonds from the polishing sludge. Since these are physical methods, they were of special interest.

Centrifuging [8]

The method uses the difference in specific gravity (and weight) for the separation of the materials involved. It is generally employed to separate solids from liquid. It is also used for separating different size particles of the same material.

For separating a solid from a liquid phase, centrifuging is carried out as follows. The suspension is placed in centrifuging bottles and subjected to rotation. Because of the centrifugal force acting on the solids, they move to the bottom of the bottles thereby effecting separation.

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For separating different sizes of particles in a powder (grading), a slurry (in a carrier as oil or water) of the powdered material is placed in centrifuging discs. Upon rotation, the larger particles are separated from the smaller ones and form rings on the disc. Rotation is carried out at a predetermined speed. The separated powders are subjected to centrifuging, at a predetermined speed to effect further separation. Thus by successive centrifuging, grading can be carried out.

Although centrifuging is a very useful technique and has been successfully used as described above, it has the following limitation: It cannot separate particles of different densities having approximately the same mass, since during centrifuging they will be subjected to the same centrifugal force. For example, a diamond particle 2 μm in diameter cannot be separated from a particle of tungsten carbide 1.2 μm in diameter because they have the same mass.

Heavy Media Separation [9-11]

This technique capitalizes on the physical property of specific gravity for separating diamond from other constituents of the sludge. This process requires selection of a liquid medium, whose density lies between that of diamond and the particles to be separated. The process consists of initially concentrating the mixture after burning the organic material. The concentrated mixture is poured into the liquid medium. The liquid is allowed to stand alone for some time at the end of which the lighter material is separated by decantation. The heavier fraction may again be subjected to the process but with a liquid medium of higher specific gravity. For example, methyl iodide with a S.G 3.3 can be used to separate diamond (S.G. 3.5) from other materials of a lower SG, such as silicon carbide (S.G. 3.2), boron carbide, glass, etc [10]. The lighter materials float while the heavier diamond sinks to the bottom. The advantage claimed by use of this method is that a significant amount of methyl iodide that gets removed with the waste material can be reclaimed. This reduces the requirements to 20% of that used without recycling methyl iodide. The float layer is poured into a Buchner funnel and the methyl iodide is pumped out using vacuum

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into a filter flask. The sink portion is also put in a Buchner funnel. The sink and the float fractions are washed with acetone in the separate Buchner funnels and the filtrate is collected in a separate flask. The powders are dried on trays. The washed liquid, called the acetone wash liquor, is either immediately or within 8 hours poured into 10 times its volume of water. Methyl iodide precipitates. The top layer is discarded and the methyl iodide layer is shaken with cold water. This is filtered through a Buchner funnel twice using dry filter paper each time, to remove any remaining waste material.

This method is used for the separateion of diamond, that is free of surface impurities, from heavier material. Antimony tribromide (S.G 4.9) has been used to separate diamond from a heavier material such as tungsten carbide and cobalt, but it is very toxic and does not offer a practical solution.

After the literature survey, the following methods were found suitable to start with, for the reasons mentioned below. In case of the polishing sludge, it is not intended to dissolve the sludge by using chemicals. Hence, when skin flotation is carried out, some impurities may be expected since fine particles of tungsten carbide-cobalt are present in the mixture. This method may be attempted to investigate its productivity.

Centrifuging may be a good method for the separation of a solid phase from the as-received sludge. It may result in the recovery of oil with a minimal effort. Also it may be possible to concentrate diamond by subjecting the sludge to centrifuging at different speeds.

For obtaining a quick estimate of the diamond content of the sludge, heavy media separation and chemical separation methods were found to be worth investigating. It is well understood that these methods use chemicals (the former, uses chemicals extensively, while the latter uses chemical that can be recycled), and therefore cannot be the solution to the problem.

Since, the literature does not state any specific method for the separation of diamond from the polishing sludge without the use of chemicals, it appears that a physical method

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may have to be developed or the available methods may have to be suitably modified to deal with the current problem.

CHAPTER 3

PROBLEM STATEMENT

In view of its high hardness and wear resistance, diamond is not expected to degenerate significantly during the polishing process. The sludge generated in the polishing of cemented tungsten carbide pen balls consists primarily of a mixture of tungsten carbide, cobalt, diamond, and a carrier oil. This sludge is currently treated as a waste generated during the polishing process and is disposed off by some industries without the recovery of diamond. The cost of diamond abrasives used per year in some polishing industries can be significant ($250,000 /year). Recovery of diamond from the polishing sludge can, therefore, result in significant savings in the polishing costs.

As discussed in the literature review, several techniques of separating diamond from the ore and from other impurities were developed in the past and applied with considerable success. These include chemical, magnetic, mechanical, electrical, and electro-chemical methods. Some of these methods may not be desirable today, in particular the methods involving the use of caustic chemicals. These methods not only are unsafe but also costly. Other methods such as magnetic and electrostatic are not suited to the type of mixture in question and the size of particles involved.

Based on the literature review, the most suitable methods for diamond recovery were first attempted. The goal is to develop a physical method for the recovery of diamond from the polishing sludge with minimal use of chemicals in general, and no caustic chemicals in particular. Oil recovery is also thought desirable not for its economic value since it can be a serious source of contamination if it is not properly disposed.

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A simple technique has been developed for the recovery of fine diamond (<=2 μm) from polishing sludge containing cemented tungsten carbide. This involves preparation of a powdered sludge, pulverization of the powdered sludge, thermal treatments, followed by decantation, filtration and distillation processes.

Scope

To develop a process suited for the reclamation of diamond from the cemented tungsten carbide polishing sludge, the problem has been divided into following steps:

i) Conducting a critical literature review to assess the various methods used for separating diamond from ores and minerals, and different types of polishing sludges, with emphasis on the recovery of diamond from polishing sludge containing cemented tungsten carbide.

ii) Investigating suitable methods, from the literature, which may be used for the separation of diamond from the polishing sludge.

iii) Performing experiments with the current methods and checking their suitability for the recovery.

iv) Based on these experiences, developing a simple physical method for the recovery of diamond with a minimum amount of chemicals in general and no caustic chemicals in particular.

v) Fabricating a laboratory scale apparatus for the recovery of diamond and oil.

vi) Initiate building a prototype equipment for the recovery of diamond and oil. This is intended not only to recover diamond and oil on a larger scale, but also on a continuous basis.

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CHAPTER 4

EXPERIMENTAL WORK

Recovery of Micron Size Diamond From Polishing Sludge

<u>Introduction</u>

Lapping of tungsten carbide balls with diamond abrasive generates polishing sludge consisting of diamond particles, tungsten carbide, cobalt, and polishing oil. Since the disposal of these constituents is a potential environmental hazard, the recovery of all the different constituents is desirable. Moreover the "safe" disposal of the sludge is not without considerable added cost, especially as the OSHA regulations become more stringent. Recovery of diamond is important and is the focus of this work. From the environmental standpoint, rather than its monetary value, recovery of oil is considered important. Recovery of oil has been dealt with later in this work, although some part of it is considered under 'preparation of sludge'. The tungsten carbide-cobalt mixture that is left after the recovery of oil and diamond may be used by the manufacturers of the cemented tungsten carbide balls as the basic raw material after checking its purity.

In the following, the characteristics and the composition of the sludge are discussed. This is followed by a description of the process of diamond recovery and the apparatus used. Following the recovery of diamond, the recovery of oil is discussed along with its apparatus. Two methods used for the recovery of oil are described and a comparison made for judging the suitability of a method for a type of as-received sludge. Two chemical methods were investigated to find the effect of chemical reagents (their effectiveness, time

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required for reaction and the suitability of existing methods when applied to the sludge). Since tungsten carbide and cobalt are left after the recovery of diamond and oil, they need not be processed further for their recovery, although, cleaning these powders may be required.

Nature of Sludge

The polishing sludge, was received from one company in 20 liter containers. Qualitative observations were made by carrying out simple experiments with an aim of understanding the nature of the sludge but not for carrying out a detailed characterization of the sludge. These experimental observations were found to be useful while carrying out the experiments for diamond and oil recovery.

Observations were made about the weight, and the how well the solid phase was dispersed in the oil. These experiments were the basis for two different routes that were taken for the recovery of oil and for sludge preparation. The weight of a one liter sample of sludge was found to vary from batch to batch due to a differing amount of solid phase present in them. The effect of settling time on the sludge was also observed. Response to a magnet, and efforts to float the oil using water (at room temperature as well as at boiling) were made. The effect of different surfactants to separate the oil from the solid particle was observed. Although different solvents, such as turpentine, gasoline, chloroform, methyl alcohol, and trichloroetylene were used in an attempt to dissolve the oil and free the solid phase, only trichloroethylene was found effective. These observations are summarized in Table I. The powdered sludge is obtained from the as-received sludge by the oil recovery and oil burn-off processes. The powdered sludge is then used to reclaim diamond by using pulverizing, decantation, filtration, and distillation processes. Then nature of the sludge influences the sludge handling process.

TABLE I

OBSERVATIONS ON THE NATURE OF THE AS-RECEIVED SLUDGE

Sl. No.	Type of Observation	Treatment /Operation	Observations and Remarks
1	Physical	Visual observation and effect of settling time (2 minutes and 8 hours)	As-received sludge is made up of a black and thin top layer and dense semi-solid bottom layer. Volume of sediment to the total volume may vary from 8% to 44%. Heavier fraction settles fast (with in 1-2 minutes. Supernatant liquid is found to be black even after 8 hours.
2	Physical	Weigh 1 liter of decanted as-received sludge	Weight is found to be ~1.54 kg. Weight of oil is 0.9 kg and the weight of solid phase is 0.64 kg.
3	Physical	For observing the response of the sludge to a magnet, a permanent magnet is brought in close vicinity to the sludge	Whole mass of oil, tungsten carbide and cobalt is found to move along with the magnet. Adding trichloroetylene resulted in a thin black supernatant fluid layer. The magnet is not found to be as effective in presence of trichloroethylene.
4	Physical	Add water	Although oil is lighter, it does not float on surface. The as-received sludge forms a bottom layer. On heating, no separation results. Heat conduction is observed to be bad and the small sludge globules are found to rise to the surface and fall back into the sludge mass, while the water body is still cold, indicating local heating

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TABLE I (Continued)

OBSERVATIONS ON THE NATURE OF AS-RECEIVED SLUDGE

Sl. No.	Type of Observation	Treatment /operation	Observations and Remarks
5	Chemical	Boil with sodium hydroxide, potassium hydroxide and ammoniacal soap solution	These surfactants were not found to have an effect on the sludge.
6	Chemical	Treated with Trichloroethylene	Oil dissolves in trichloroethylene. Sludge mass appears loose. The supernatant liquid is black in color indicating suspension of tungsten carbide particles.

Experiments with Current Methods

Introduction

Based on the review of the literature on diamond recovery the following four techniques were considered in the investigation initially: centrifuging, heavy media separation, skin flotation, and chemical separation. The goal of this investigation was to assess these techniques and based on it find a simple physical technique for the recovery of diamond without the use of caustic chemicals. The rationale for the selection of these four techniques is as follows:

1. Heavy media separation was investigated since it is a very simple but sure method of separating different density powders.

2. Centrifuging was attempted since it is known to separate solid phase from liquid phase in a suspension and for separating powders of different densities.

3. The skin flotation method is primarily used for the recovery of small size particles. It is also characterized by the use of a small amount of non-caustic chemicals. Hence, this method was attempted to determine the yield.

4. The principle reason for attempting chemical methods was to obtain a quantitative estimate of the diamond present in the sludge. This may also provide an opportunity to determine the response of the sludge to various chemicals. The diamond contained in the sludge was expected to be $<= 2$ μm. Hence, chemical methods, such as 'fusion with caustic alkali ' and 'oxidation under heat followed by alkali treatment' were not used since the former requires prolonged (4 to 5 hours) heating at ~500 °C, while the latter requires heating at ~900 °C resulting in a loss of fine diamond. This becomes an important factor in the case of the sludge in question. Hence, the acid dissolution method was the only chemical method used.

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In the following, the results of the above techniques will be summarized. Based on this experience a new technique was developed which will be discussed subsequently.

Experimental Work and Test Results

Heavy Media Separation: Heavy media separation was used with methylene iodide (S.G. 3.3) in a wax bath (melting point 60 °C) as the separating fluid. However, the cost of methyl iodide and the considerable amount of fumes associated with it make it difficult to consider it as an economically feasible and safe method for separation. Moreover, the particles associated are too fine and do not separate effectively unlike those involved in the extraction of the diamond from minerals.

Centrifuging: The reason for selecting this technique was to separate the heavier and lighter constituents in the sludge from the oil. Further, as there exist considerable differences in the densities of the constituents, it was thought that a specific speed would separate the tungsten carbide and cobalt particles from diamond. Tests were carried out at different speeds (100, 200, 400, 800, 1600, 3200, and 4000 rpm) which resulted in a thick black mass at the bottom of the centrifuging bottle and a thin black suspension. The settled mass when heated for evaporating the residual oil resulted in a hard black solid.

Thus, centrifuging was ineffective in settling the tungsten carbide and cobalt from the oil due to the fine particles forming a colloidal solution. It could not be employed for separating diamond from other majority constituents not only because the particles involved are too small but also because the diamond particles have active surfaces that interact with the oil thereby holding the diamonds in suspension.

Skin Flotation Method: Since the sludge contains very fine diamond, the skin flotation method was considered as a candidate method. Also, the small quantities of chemicals used in this method made it worth investigating. The purpose of the tests performed here was to investigate how effectively the diamond present in the sludge can be separated and made to float when suitably conditioned with reagents.

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About 50 grams of dry pulverized sludge was taken in a glass beaker. To this, 100 ml of potassium hydroxide solution was added (made by dissolving 15 grams of potassium hydroxide powder in water so as to make the 100 ml mixture). The mixture of sludge and potassium hydroxide was heated for 3 to 5 minutes to its boiling point. Ammoniacal soap solution, mixed with oleic acid, was then added. The ammoniacal soap solution was made by taking dilute soap solution (50 ml, commercial quality) to which ammonium hydroxide (10 ml, 28% w/w) was added. The ammoniacal soap solution was added to the sludge treated with potassium hydroxide. The mixture was stirred thoroughly and a few drops (3 to 4) of oleic acid were added. Distilled water was then added to the mixture to make 500 ml. The beaker was then kept at an angle and gently stirred with a glass rod. The diamond particles formed a thin layer at the surface of the water. This layer was decanted in another beaker. Unfortunately, the amount of powder collected by the skin flotation method was very small (0.1 gram). Diamond powder appeared gray and suggested the presence of some tungsten carbide/cobalt powder as an impurity.

The following conclusions can be drawn from the above tests:

1. The quantity of diamond recovered by this process is low. Hence, this method may not be suitable for use in industry.

2. Impurities such as oleic acid and tungsten carbide may be present.

Acid Dissolution Method: This method was used to determine how the powdered sludge reacts with strong chemicals, such as concentrated nitric acid and hydrofluoric acids. The action on dry lumps, on dry powdered sludge, and on dry pulverized sludge was observed when they were attacked by strong chemicals over short and long durations of time. The effect of heat was also investigated on the reaction mixture.

The action of these acids on dry lumps of the sludge was observed to be rather slow. The reaction was found to cease after a few minutes. The lumps were not completely dissolved. Heating did not have any significant effect either. Increasing the surface area was finally attempted by breaking them into powder by milling. The powdered dry sludge

was well attacked while the larger particles in the powder (~ 0.25 to 0.5 mm) were not attacked. Pulverizing was found to increase the reaction rate significantly and no untreated residue was found. It was, therefore, concluded that an effective treatment requires pulverization.

About 100 grams of powdered sludge was taken in a 2 liter beaker. Concentrated nitric acid (71% w /w) was slowly added resulting in vigorous and exothermic reaction. Thick brown fumes were immediately observed. A five fold increase in the volume of the reaction mixture was noted. Hence it was necessary to contain the reaction mixture in a large vessel (7 to 9 times the volume of the reaction mixture). Addition of the acid was continued slowly while waiting for the reaction to subside, with a further addition of concentrated nitric acid. Approximately 400 ml of nitric acid was required to dissolve 100 grams of the sludge.

After centrifuging at 3000 rpm for 4 minutes, a clear solution of reddish-brown color was separated. Decantation was carried out to remove the supernatant fluid. This was then treated with a mixture of nitric acid (100 ml) and hydrofluoric acid (400 ml) in the ratio of 1: 4. This reaction was not vigorous and was allowed to stand for 24 to 40 hours.

A gray precipitate was observed after centrifuging (centrifuging was carried out to separate the solids from the liquid). The precipitate was washed with water and centrifuged. The precipitate contained diamond mixture weighing ≈ 20 grams.

The following conclusions can be drawn from the above experiments :

    i. Dry un-powdered sludge was attacked slowly and some mass remained unattacked.

    ii. Approximately 25 hours were required for the completion of the reaction when pulverized sludge was used.

    iii. Even the caustic chemicals were not found to be effective on dry pulverized sludge.

The following conclusions may be drawn after conducting various tests on the polishing sludge, using the initially chosen four techniques :

Even the caustic chemicals take considerable time to react with the polishing sludge and hence chemical separation is not an effective alternative for industrial recovery of diamond from the polishing sludge. The skin flotation process, although suitable for the recovery of fine diamond, does not appear to be a feasible alternative for industrial applications because of the low yield. Heavy media separation requires toxic materials to be used as the media, hence it can be a health hazard. Centrifuging alone is not found to be effective due to the small particle size of all the powders involved with polishing sludge. This lead to the need for the development of a new simple physical method for the recovery of diamond.

New Method of Recovery of Diamond Particles from Polishing Sludge

Introduction

As indicated earlier, the thrust of this project is to develop a physical method of diamond recovery that would use a minimum amount of chemicals. It would be ideal to be to reclaim all the ingredients in the sludge, namely, diamond, oil, tungsten carbide, and cobalt, and to be able to process the polishing sludge continuously in order to obtain high recovery rates. The principle, the process, and the equipment built for diamond recovery are described in the following sections and explained with the help of flowcharts and circuit diagrams.

Principle of the Diamond Recovery Process

The process aims at using the differences in the specific gravity of diamond and tungsten carbide-cobalt mixture, their differences in the coefficients of thermal expansions, and the adhesive forces between particles of different materials in a fluid in order to allow the separation of diamond from the sludge. Physical processes such as decantation,

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filtration, distillation, quenching, and pulverizing are employed to achieve the recovery. The as-received sludge was first processed for oil recovery and for the preparation of powdered sludge. The powdered sludge was thermally treated to remove traces of oil and pulverized before it was subjected to a quenching treatment. The pulverized and quenched sludge was mixed with water, followed by decantation and filtration processes. The filtrate was distilled to concentrate the solution to approximately 1/20 the original filtrate volume. Attempts were made to ensure that no hazardous chemicals were used.

Diamond Recovery Process

The diamond recovery process may be divided into two distinct parts. The first part deals with the processing of the as-received sludge for obtaining powdered sludge (Figure 1). This process is associated with the recovery of oil. The second part deals with the recovery of diamond. It uses the powdered sludge obtained from the first part. Thermal treatment and thermal-pulverizing (T-P) treatment then follow to condition the sludge for the diamond recovery process. Quenching the pulverized sludge followed by decantation, filtration, and distillation processes leads to the recovery of diamond.

Figure 1 shows the Flowcharts A and B for the recovery of oil and for the preparation of powdered sludge from the as-received sludge. Flowchart A in Figure 2 gives an outline of the thermal treatment process and the combined thermal treatment-pulverizing process (T-P process) used for diamond recovery from the powdered sludge. The T-P process was used often, as shown in Flowchart B in Figure 2. Flowchart A is discussed first, to give details of how the thermal treatment processes were carried out. Flowchart B in Figure 2 depicts how the thermally treated sludge was used to obtain diamond powder.

The thermal treatment of the powdered sludge for diamond recovery aims at removing the oil traces from the powdered sludge (which is obtained by treating the as-received sludge as shown in the Flowcharts in Figure 1) and to release diamond prior to filtration. To ensure this, the thermal treatment and the T-P process were used.

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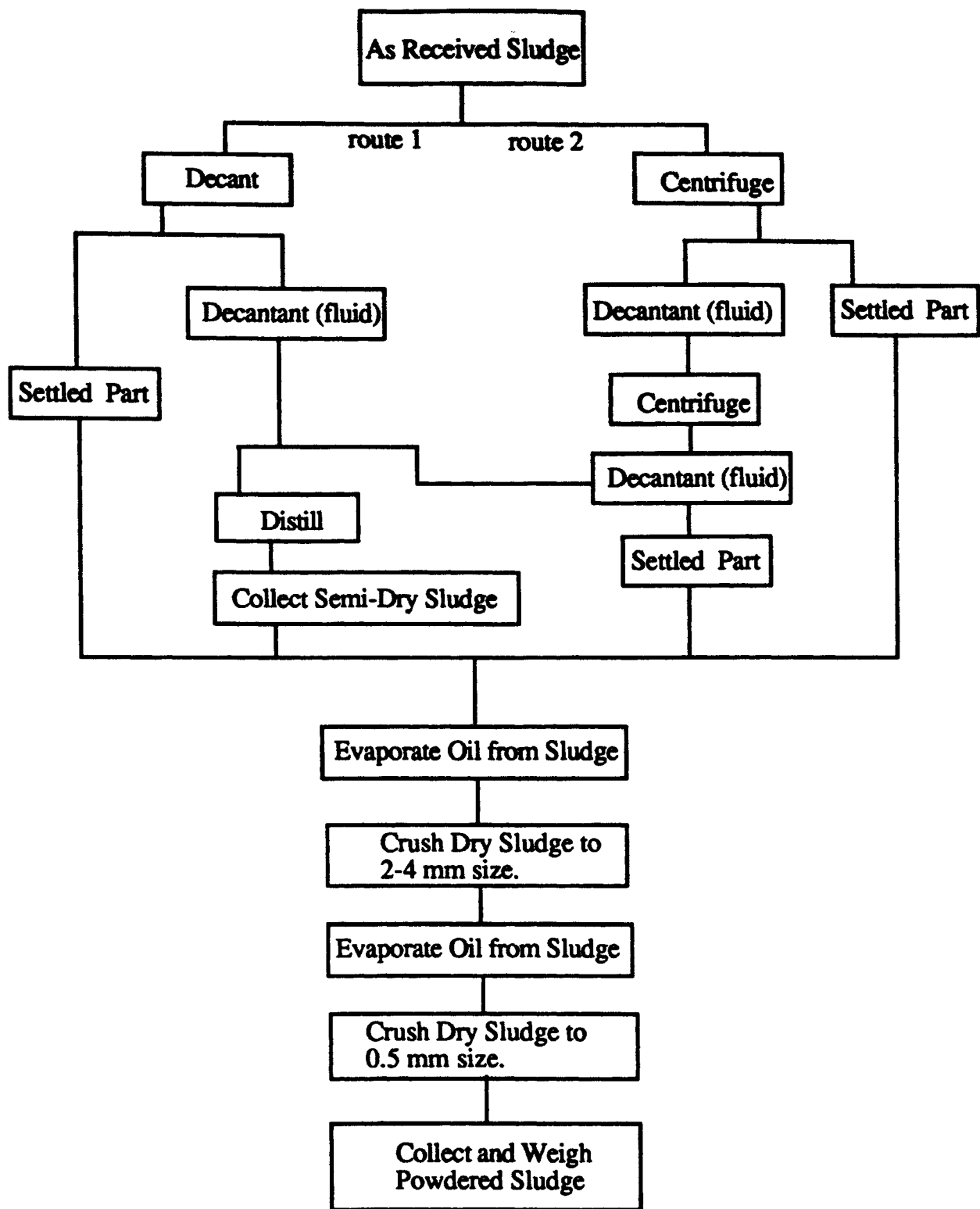
Figure 1 : Flowchart A : Treatment of as Received Sludge for Oil Recovery
and for Obtaining Powdered Sludge.
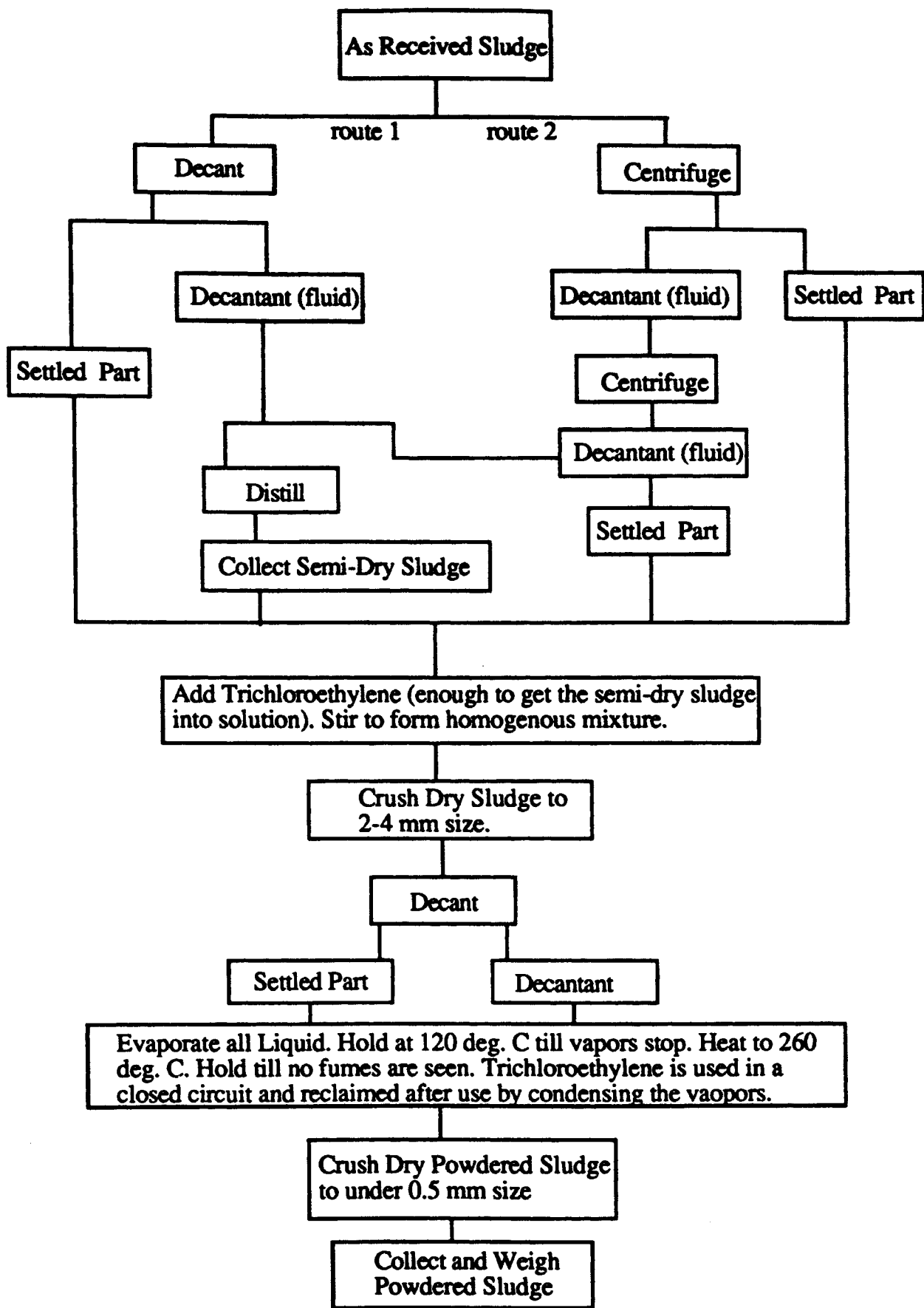
Figure 1 : Flowchart B: Treatment of As-Received Sludge for Oil Recovery and for Obtaining Powdered Sludge : Improvement over Flowchart A

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```
┌─────────────────┐
│ Powdered Sludge │
└─────────────────┘
         │
┌──────────────────────────────────────────────────────┐
│ Heat to 120 deg. C, hold for few minutes. Heat to 260 │
│ deg. C, hold for 3 minutes. Heat to 350 degree C,     │
│ hold for 2 minutes (Thermal Treatment -conducted once │
│ before the diamond recovery process)                  │
└──────────────────────────────────────────────────────┘
```

Heat to 120 deg. C, hold for few minutes. Heat to 260 deg. C, hold for 3 minutes. Heat to 350 degree C, hold for 2 minutes (Thermal Treatment -conducted once before the diamond recovery process)

┌───────────┐
│ Pulverize │
└───────────┘

Heat to 450 deg. C in vacuum or inert atmosphere, stir while heating, hold for 3 minutes

Quench in water held at 0 deg. C

T-P treatment

Figure 2: Flowchart A: Thermal Treatment and T-P
Treatment Processes

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                    ┌─────────────────────┐
                    │  Powdered Sludge     │
                    └─────────────────────┘
                               │
                    ┌─────────────────────┐
                    │  Thermal treatment   │
                    └─────────────────────┘
                               │        ◄──────────────────────────────┐
                    ┌─────────────────────┐                            │
                    │   T-P treatment      │                            │
                    └─────────────────────┘                            │
                               │        ◄──────────────────────┐       │
                    ┌─────────────────────┐                    │       │
                    │ Mix with water and stir│                  │       │
                    └─────────────────────┘                    │       │
                               │                               │       │
                    ┌─────────────────────┐                    │       │
                    │       Decant         │                    │       │
                    └─────────────────────┘                    │       │
                     │                    │                     │       │
            ┌───────────────┐      ┌───────────────┐            │       │
            │  Decantant    │      │  Settled Part │            │       │
            └───────────────┘      └───────────────┘            │       │
                    │                      │          Yes       │       │
            ┌───────────────┐      ┌───────────────┐────────────┘       │
            │    Filter     │      │   If n<=4     │                    │
            └───────────────┘      └───────────────┘                    │
             │              │               │ No                        │
    ┌─────────────────┐     │      ┌──────────────────────┐   Yes       │
    │ Collect powder  │     │      │ If Weight >1/10 of   │─────────────┘
    │ on filter paper │     │      │ Original Weight      │
    └─────────────────┘     │      └──────────────────────┘
                    ┌───────────────┐        │ No
                    │   Filtrate    │   ┌───────────────┐
                    └───────────────┘   │ Collect Powder│
                            │           └───────────────┘
                ┌─────────────────────┐
                │ Distill and Collect │
                │  Diamond Powder     │
                └─────────────────────┘
                            │
                ┌─────────────────────┐
                │ Clean, Weigh and Store│
                │  Diamond Powder     │
                └─────────────────────┘
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Figure 2 : Flowchart B : The Diamond Recovery Process

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In the following sections, the details of the process will be discussed.

Thermal Treatment Process: Powdered sludge of ~100 grams was heated at a slow rate. The temperature was first maintained at 120 °C for 5 minute to evaporate water. The powdered sludge was stirred intermittently to ensure uniform temperature. It was further heated to ~250 °C (since the boiling point of the oil is 240 °C) until the fumes stopped coming out from the powdered sludge. Stirring was continued duri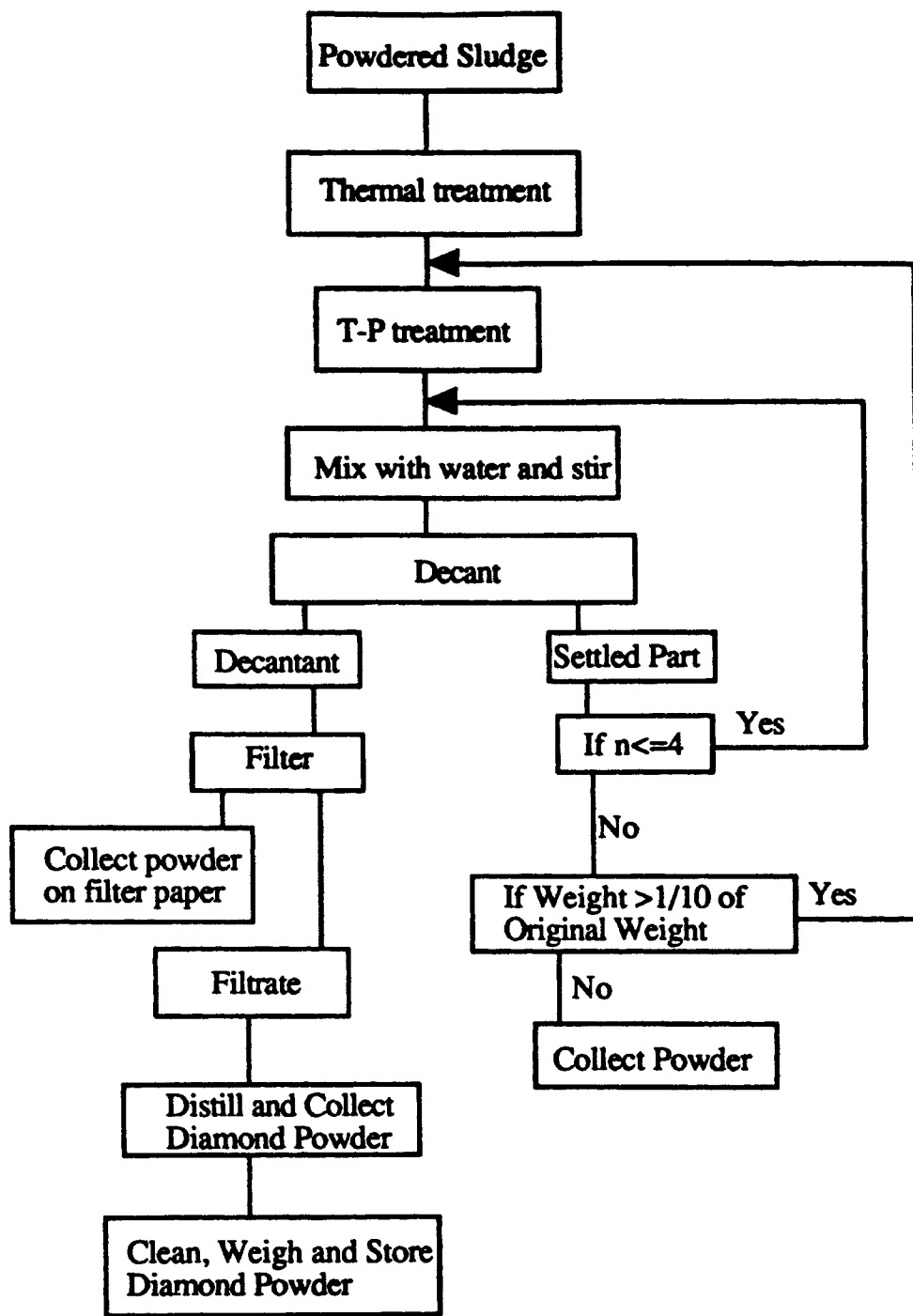ng the process. It was then heated to ~350 °C to ensure complete oil removal which was followed by the pulverizing process. The fumes of oil were condensed and collected.

Thermal Treatment-Pulverising (T-P) Process: The pulverizing operation is considered an important step in the T-P process. For the laboratory scale demonstration of the diamond recovery an agate mortar and pestle were used to pulverize the powdered sludge. However for large-scale prototype, a ball mill is recommended. About 10 grams of the powdered sludge was used each time in the mortar and pestle and they were pulverized manually until a fine powder was obtained. Thus, all of the 100 grams of powdered sludge was pulverized. This process was followed by a controlled thermal treatment. The thermal treatment process involves heating the pulverized sludge to 450 °C and holding it at this temperature for ~5 minutes while stirring to ensure a uniform temperature. The hot pulverized sludge was then quenched into a 2 liter beaker filled with water kept at 0 °C. This treatment acted as a thermal shock on the powdered sludge which was used to break the diamonds free from the rest of the adhering mass (tungsten carbide-cobalt mixture) because of the significant difference in the coefficients of thermal expansion of diamond (0.8×10^{-6} /°C), and the tungsten carbide (5.2×10^{-6} /°C), and cobalt (12×10^{-6} /°C) mixture. The temperature of the water was observed to rise by 8 to 10 °C as a result of the addition of the sludge.

Decantation Process: The pulverized sludge in water consists of tungsten carbide, cobalt, and diamonds which are separated due to thermal shock. Further separation of diamonds would depend on bringing the diamonds to a suspension and at the same time

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allowing tungsten carbide and cobalt to settle. Thus, decantation plays a very important role and has been extensively employed in this investigation thus warranting a separate discussion.

Typically, a stirred pulverized sludge-water mixture, if allowed to settle, would yield different concentrations of diamond in the suspension for different periods of settling time. This principle is employed in designing the decantation process. The Flowchart in Figure 2 illustrates the decantation sequence employed.

After allowing the pulverized sludge to settle for 1 minute, it was carefully decanted into 2 glass beakers. The number of decantation operations performed is indicated by a counter n which becomes an important variable as the concentration of diamond during any decantation is found to depend on it. After the T-P treatment, the amount of fine particles in suspension are found to be much more than those after a few decantations. For the first two decantations, the concentration of the particles was found to be very high. Hence, the decantant (2 liters, one in each beaker) was diluted to double the volume. Dilution was employed since high concentration of fine particles would tend to obstruct the pores of the filter paper and retain diamond on it. After dilution, the suspension in each beaker was allowed to settle for ~4 to 6 minutes (for n=1 or n=2). This ensured that only the particles that lie in the range up to approximately 3 μm remained in suspension. Optical microscopy of the samples was used as a basis for determining this time period range. A drop of supernatant liquid was drawn every one minute and the size of the particles present were noted. Decantation slides showed that immediately after stirring, large particles in the 40 to 60 μm range were found in considerable quantities. After allowing the 4 to 6 minutes settling time, particles of this size are found to be completely eliminated. Decantation was carried out and decantant collected in a 4 liter container. The decantant was used as the input to the filter which used a 2.7μm pore size filter paper.

To the settled part of the pulverized sludge (refer to the Flowchart B in Figure 2) obtained from decantation (n=2), an additional two liters of water was added and the

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counter was increased by 1, and decantation was carried out as explained in the flowchart (allowing 1 to 2 minutes settling time). However, since n > 2 the dilution process was stopped (concentration of small particles decreases with each decantation process). The decantant was then fed to the filter. Four decantations were carried out (until n=4) before the pulverized sludge was again subjected to the T-P treatment. This number of decantations that should be made before carrying out the next T-P treatment was arrived at after numerous experiments. After n=4 the yield of diamond powder was usually found to drop off and stagnate at a low value.

Filtration Process : The decantation process was followed by the filtration process. Filtration was carried out under a low vacuum (500 to 600 mm of mercury column). Vacuum was used to pump the filtrate to the boiler to avoid contamination. A floating indicator facilitated the measurement of time for every 100 cc of fluid being filtered. During the filtration process, the diamond were allowed through the filter paper while other elements (tungsten carbide and cobalt) stay on the filter paper. This could be due to the comparatively low bond strength between diamond and water. Since water bonds to tungsten carbide and cobalt better, this appears to be the reason for the tungsten carbide and cobalt particles to be weakly held on the filter paper, while diamond particles which are not bonded to either each other or to the tungsten carbide or cobalt, flow with the water.

Distillation Process: Distillation was carried out to concentrate the filtrate. The boiler was held under vacuum to facilitate the evaporation of water at lower temperature. The distillation process was carried out at ~85 °C and the filtrate was concentrated. The time taken for concentration was found to be one hour and 45 minutes, when a 2 liter filtrate was processed using a 1 kW heater. Once the filtrate was concentrated to approximately 50 ml, heating was stopped. The concentrate was transferred to an open petridish and heated on a low power (about 200 Watts) heating coil until all the water evaporated leaving diamond powder on the petridish. The powder was found to be light brown in color.

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The settled part of the pulverized sludge was treated as shown in the Flowchart B in Figure 2. The T-P treatment, decantation, filtration, concentration, and the evaporation processes were carried out as shown in the flowchart until approximately 1/10 of the weight of the original pulverized sludge was left. The pulverized sludge from the top of the filter paper was collected in a separate beaker for analysis and further treatment. This treatment was carried out in the same way as shown in the flowcharts of Figure 2, after a sufficient amount of sludge was collected.

Equipment for the Diamond Recovery Process

Figure 3 is the circuit showing the different elements used in the process. The elements in the circuit are described below.

Pulverizing Unit: The pulverizing unit is used to crush the powdered sludge after the removal of traces of oil so as to allow more surface area to be exposed to heat. It is also used for the effective release of the diamond particles from the larger aggregates after the T-P treatment process.

In the experiments conducted, mortar and pestle was used to hand grind the sludge since the quantity of sludge being handled was small (10 grams at a time). For processing larger quantities, a pulverizing unit, such as a ball mill, is a requirement.

Filter: The filter was used under a vacuum (in the range of 500 to 600 mm mercury). It was built to accommodate an 11 cm diameter of filter paper. The filter paper is supported on a perforated disc (approximately 100 holes of 1 mm diameter, were made on an 11.5 cm diameter disc), which sits on an O-ring inside the filter. The filter has a 2 liter capacity. To lead the filtrate to the boiler, the filter outlet was connected to the boiler inlet port.

Boiler : The boiler is an aluminum pressure vessel with a four liter capacity. It has an inlet port connected to the filter outlet port, an outlet port connected to the condenser coil, a port for a thermometer and a port for a stirrer.

Condenser: The condenser consists of a condensing coil made from 4 m of 12 mm copper tubing. The condenser coil is immersed in running water at ambient temperature

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Figure 3 : Apparatus for Diamond Recovery
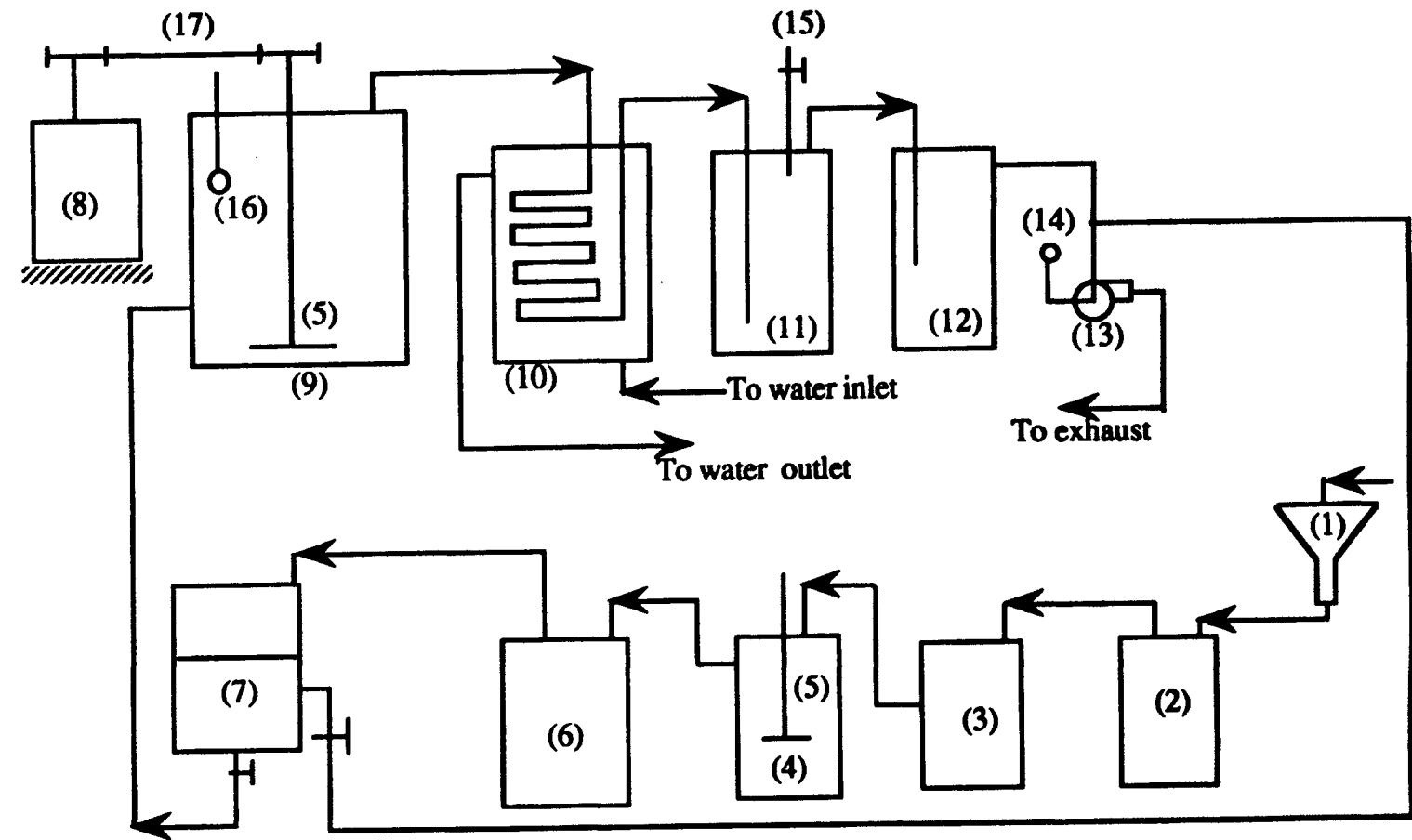
1) Pulverising Unit   2) Quench Tank   3) Mixing Tank   4) and 6) Decantation Tanks   5) Stirrer
7) Filter   8) Motor   9) Boiler   10) Condenser   11) Collection Tank
12) Vapor Trap   13) Pump   14) Pressure Gauge 15) Breather valve   16) Thermometer
17) Speed Reducer

(20 °C). The inflow of ~ 500 ml of water per minute was found satisfactory as an increase in temperature noted over 3 hours was only 6 °C.

Collecting vessel: The condenser coil leads to the collection vessel (a conical flask was used for the purpose). This had a rubber stopper with two holes, one for inlet of a steam/water mixture (through the condenser coil) and the other to allow air to flow in through the breather valve, when the flask needed to be emptied. A port from the conical flask (situated 200 to 250 mm above the level of liquid, to avoid bubbles entering the vacuum line) was connected to the vacuum line (pump usually working at 400 rpm, 500 to 600 mm of Hg).

Oil Recovery Process

Objective of the Oil Recovery Process

The polishing sludge contains a large fraction (70% by volume) of oil in the mixture. The objective of the oil recovery process is to recover most of the oil, including the heaviest fraction, so as to regain the same (or almost the same) composition of oil used in polishing. Recovery of oil not only enables its reuse for polishing application (the savings here are probably minimal) but also addresses the environmental issues namely disposal of the oil waste. OSHA regulations and environmental concerns strongly suggest the recovery of oil as a by-product instead of discarding it as a waste. In the process developed here, it is not a separate step but a part of the process for the diamond recovery and comes out as a bi-product.

Preliminary Efforts for Separation of Oil from the As-Received Sludge

The constituents of sludge are suspended in oil (the heavier fraction of the sludge settles, but is well dispersed in oil). For recovery of diamond from the polishing sludge, the removal of oil is therefore a very important factor. The effect of surfactants such as soap solutions, oleic acid, and solutions of sodium and potassium hydroxide in water have

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been observed. These have been attempted under low and high concentrations but to no avail. Boiling with these reagents also proved to be ineffective. Boiling the mixture of the as received polishing sludge with a reagent was ineffective because of poor heat transfer. The polishing sludge was therefore added to the solution of these reagents in boiling water but no significant effect was noticed. A distillation process was finally resorted to, because of the special characteristics of the as-received sludge.

Methods for the Separation of Oil from the As-Received Polishing Sludge

The as-received sludge has some inherent characteristics that make it difficult to process for distillation. The solid phase constituting the physical mixture is very heavy (tungsten carbide has S.G. ~ 15.5 and cobalt has S.G. ~ 9). The particles are fine and well dispersed in the oil making it a homogeneous mixture (the settled sludge forms a semisolid phase, but the suspension remains black even when stored for days). The as-received sludge was treated by two different methods before distillation. These two methods are first described and then compared to bring out their merits. A brief description of the equipment and the process is also given here.

The first method (gravity method) uses the force due to gravity for the separation of the heavier fraction from the rest of the suspension. The second method (gravity + centrifuging), uses centrifugal force in addition to the gravitational force for separating the heavier fraction of the sludge from the rest. These two methods involve distillation and condensation processes for the separation and collection of oil from the as-received sludge.

Gravitational Method: This method is depicted in Flowchart A (route 1) of Figure 1. The as-received polishing sludge in a 20 liter container was thoroughly mixed by stirring. One liter of the as-received polishing sludge was allowed to stand for 3 hours to settle out the heavier sediments. Decantation was carried out and the settled part (which appeared loose due to the presence of oil) was separated. The decantant was then distilled. During distillation, the decantant was heated in a boiler to ~80 °C. The first fraction of the distilled oil was found to be transparent. The volume of this fraction was approximately 300 ml.

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Heating to higher temperatures resulted in the separation of a second fraction. A pale yellow fraction evaporated at a higher temperature (~150 °C) and ~250 ml of oil was collected. A third distinct fraction of oil, which appeared dark yellow or faint brown in color was collected at ~200 °C (~100 ml of oil). The final fraction of ~60 ml of thick dark brown liquid was distilled at temperatures in the range of 250 to 270 °C. Heating was stopped when the sludge mass in the boiler became semi-dry. Although all the oil was collected in one flask in the present investigation, it is possible to collect different fractions separately if that is desired.

The settled part (refer to the Flowchart A in Figure 1) was collected separately and mixed with the semi-dry sludge obtained after the distillation process. This was then heated at ~270 °C to evaporate all the oil. The heating process yielded dry lumps of the sludge which were crushed to a powder (average size particles 2 to 4 mm). It was heated to ~270 °C and stirred to ensure homogenization of temperature. The powdered sludge was weighed and stored carefully to prevent moisture contamination.

Gravitation and Centrifuging Method: In this method, depicted in Flowchart A (route 2) in Figure 1, a 1000 ml of well stirred as-received sludge was taken in a beaker and then distributed equally in two centrifuge bottles. These were centrifuged at 4000 rpm for 5 minutes. The supernatant fluid was collected by decantation. The supernatant fluid was taken in two fresh centrifuge bottles and centrifuged again. The settled part was mixed with the one obtained from the first centrifiging process. When 1000 ml of fluid, weighing 1.63 kg, was taken and centrifuged as stated above, a total of 0.74 kg of thick sludge was separated from the fluid. The supernatant fluid was found to be black indicating that it still contained finely divided tungsten carbide cobalt particles along with diamond. The supernatant fluid was decanted and distilled in the same way as in the gravity method. The settled part was collected separately and mixed with the semi-dry sludge obtained after the distillation process. These were subjected to heating at ~270 °C

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and crushed as in the gravity method. The settled part of the centrifuged sludge has much lower oil content than the settled part of the sludge from the gravity method.

Although the gravity method is cheaper (since the capital and maintenance costs for the centrifuge are not involved), the ~7% fall in the quantity of the recovered oil can be an important considerations. The difficulty in stirring the as-received sludge during the distillation process also warrants a larger motor than that used in the centrifuging method.

Results of Oil Recovery Process

The quantitative recovery of oil depends on the quality of the sludge being used. The oil recovery made (following the Route 1 in the Flowchart A in Figure 1) without centrifuging resulted in 700 ml of oil, while, the oil recovery (following Route 2 in the Flowchart A in Figure 1) without centrifuging resulted in 750 ml of oil.

Equipment Used for the Oil Recovery Process

Figure 4 shows important elements used in the oil recovery process. They include a boiler, stirrer, condenser and an oil collection vessel. These are briefly described in the following after which the process details are discussed.

Boiler : This is an aluminum vessel with a lid to form a closed chamber. The vessel has an outlet for the removal of oil vapors. One opening at the center is to accommodate a stirrer. A leak proof joint was ensured between the lid and vessel by providing a gasket. Mechanical clamping was used to ensure a leak proof pressure vessel. Since rubber gaskets do not last longer than two or three usages, a teflon gasket was used. This is because teflon can withstand temperatures in the range of 250 to 300 °C.

Stirrer : A stirrer was mounted on the motor shaft with a flexible connector (PVC tube) which served as a flexible coupling. No positive clamping was employed to link the connector to the shaft. This arrangement provided friction drive and ensured the safety of the motor in case the stirrer failed to rotate because of the heavy sludge.

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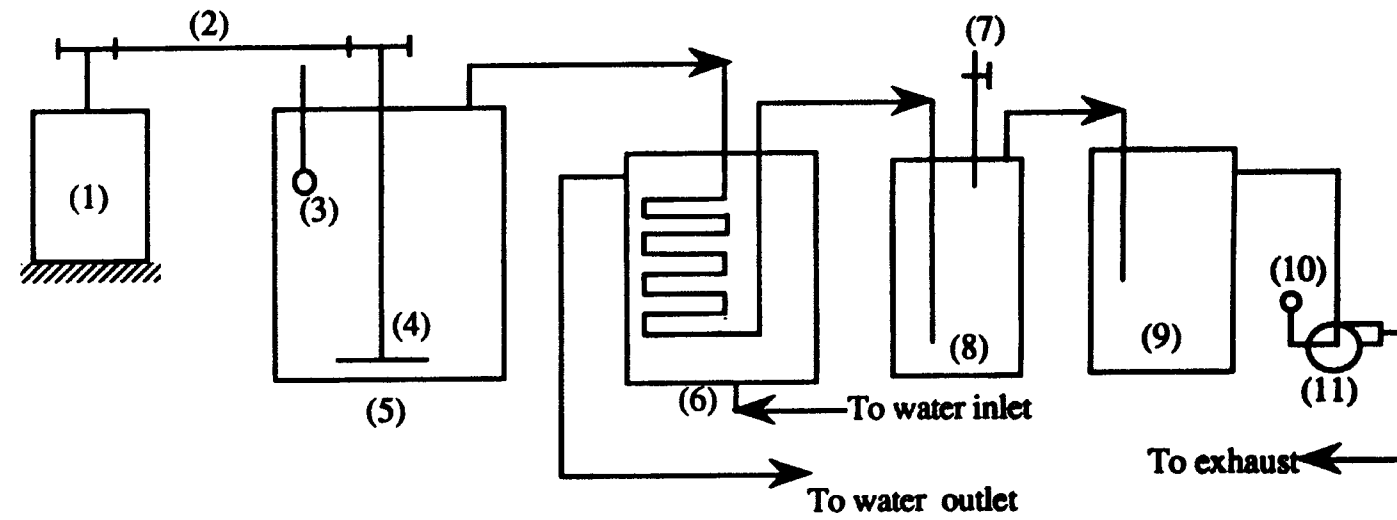
1) Motor   4) Stirrer   7) Breather Valve   10) Vacuum Gauge
2) Reducer   5) Boiler   8) Collection Tank   11) Pump
3) Thermometer   6) Condenser   9) Vapor Trap

Figure 4 : Apparatus for Oil Recovery

<u>Stirrer motor</u> :   A 1/3 Hp (72 rpm) AC motor mounted on a stand was used. Speed of the motor was controlled using a variac (0 to 100% of 115 Volt) to control splashing of the sludge in the container. Low speeds of stirring were found suitable.

<u>Condenser</u> : A cross flow condenser consisting of a 12 mm diameter copper tube turned into a coil of 50 mm diameter, was used. The coil had 25 turns and was immersed in a water tank in which a constant flow of water was maintained at approximately 700 ml per minute. The condenser was a cross flow heat exchanger to ensure effective and rapid heat transfer between the cold water stream and the hot oil vapors.

<u>Oil Collection Vessel</u> : This vessel was connected directly to the vacuum pump (1/3 Hp, belt driven, 400 rpm). The vacuum was maintained to act on the fluid level in the vessel. It allowed the evacuation of circuit of gases and the maintenance of low pressure in the circuit. The column of fluid also ensured the complete condensation of the oil in the condensation flask. It , therefore, prevented any mist from entering the pump.

<u>Improvements in the Preparation of the Powdered Sludge</u>

The process described in the Flowchart A in Figure 1 facilitates the recovery of oil, and the preparation of powdered sludge. In this process, when the oil separation is completed, a cake of semi-dry sludge is produced which does not easily crumble. It requires a thorough pulverization to be converted to a homogeneous powder. Although pulverizing may produce the desired results, it would take more time. For manual grinding, it was found difficult to obtain a fine powder from this hard dry sludge. The process was improved by treating the semi-dry sludge (just after distillation and before heating at point 1) as in the Flowchart B in Figure 1 with a small quantity of trichloroethylene. About 50 ml of trichloroethylene was added to approximately 50 ml by volume of the semi-dry sludge. The intention was to dissolve the oil which holds the tungsten carbide-diamond-cobalt particles. The mixture was stirred and allowed to settle. The supernatant black and thin fluid was decanted (this fluid may be fractionally distilled to get back trichloroethylene which may be recirculated).

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When heated to remove the traces of oil and trichloroethylene, the resulting sludge was found to be loose and it tended to crumble easily as compared to the previous dry sludge that was obtained by heating the semi-dry sludge. The 50 grams of semi-dry sludge treated thus resulted in 46 grams of powder. An additional 14 grams was obtained by heating the decantant (trichloroethylene-oil-sludge mixture). The powder was then pulverized (as shown in Flowchart B in Figure 1) and was ready for further treatment.

Trichloroethylene is used in a closed circuit and the fumes generated are condensed. The condensed trichloroethylene is recycled and used for treating next batch of sludge. It may be noted that this process is not a requirement and it does not affect the oil recovery or diamond recovery process, especially if a ball mill is used to crush the powdered sludge. It facilitates the crushing process, thereby resulting in a more effective release of diamond. When used in a closed circuit, the trichloroethylene is contained and hence not hazardous.

Experimental Design and Test Results

Experiments were conducted to understand the nature of the suspension of the powdered sludge in water, the filtrate, and the effect of centrifuging on the filtrate and the decantant. Effect of the T-P process, different filter paper areas and pore sizes on the filtration process and yield were studied. To compare the standard diamond powders with the recovered diamonds, observations were made in a scanning electron microscope (SEM) and an optical microscope. These are discussed here along with the findings and the conclusions.

Experiments on Decantation Process

A suitable time for settling of the agglomerates of cemented tungsten carbide is critical because the supernatant fluid contains individual or small aggregates of diamonds that have been released as a result of T-P treatment. The particles and agglomerates observed may be classified as follows:

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1. agglomerates of diamond, tungsten carbide, and cobalt

2. agglomerates of diamond that are present in the abrasive paste (these may not separate under the action of the thermal shock but may be separated from each other by pulverizing)

3. agglomerates of tungsten carbide and cobalt, and

4. individual diamonds.

A short settling time would result in large aggregates in the decantant that would block the filter pores and result in ineffective filtration. A long settling time would result in the settling of diamond aggregates. To find the correct range of settling time, decantations carried out before and after the T-P process, samples of decantant were taken at predetermined intervals of time and observed.

A scanning electron microscope (SEM) analysis of the decantant was carried out and the observations are listed in Table II for the decantant before the T-P treatment and in Table III for the decantant after the T-P treatment. From the SEM micrographs (Figure 5) and Tables II and III it may be concluded that 1 to 2 minutes are sufficient before the T-P process and 4-6 minutes are sufficient just after the T-P process. The first 2-3 filtrations are found to involve fine particles while after the 5th decantation the amount of fine particles are found to decrease significantly.

Experiments using Centrifuging Process

Separation of diamond from the decantant can be brought about using centrifuging, since the process can separate different density particles. With this in mind experiments were conducted at different rpms to find a suitable range. The particles sizes involved are

TABLE II

OBSERVATIONS ON THE DECANTATION PROCESS
BEFORE T-P TREATMENT (SAMPLE AO)

Photograph Number and Magnification	Decantation Time (minutes)	Characterisc Aggregate Size (μm)	Largest Agglomerate Size (μm)	Comments
D1, X100	Zero	40-60	90-100	Particles are predominantly 3 dimensional and have granular surface. Even the smaller particles (10-20 μm) have a pronounced 3rd dimension)
D2, X100	0.5	15-25	30	Notable change observed in the particle size. The 3rd dimension is still clearly seen.
D3, X100	1.5	5-7	15-25	Very few larger particles are observed
D4, X100	3.5	up to 5	10-15	Very few larger particles are observed

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TABLE III

OBSERVATIONS ON THE DECANTATION PROCESS
AFTER T-P TREATMENT (SAMPLE AP)

Photograph Number and Magnification	Decantation Time (minutes)	Characteristic Agglomerate Size (μm)	Largest Agglomerate Size (μm)	Comments
D11, X100	0.5	80-100	125-150	The particles appear to be predominantly plannar aggregates as against the predominantly 3 D particles. This may be due to pulverising process.
D12, X100	1.5	50-75	90	Notable change observed in the particle aggregate size. 125-150 μm particle aggregates are not found to be present at all.
D13, X100	2.5	25-40	70-80	Very few large aggregates (70-80 μm) are observed
D14, X100	4.5	15-35	70-80	Very few larger aggregates (70-80 μm) are observed
D15, X100	6.5	upto 10	40-50	Few larger aggregates (40-50 μm) are observed

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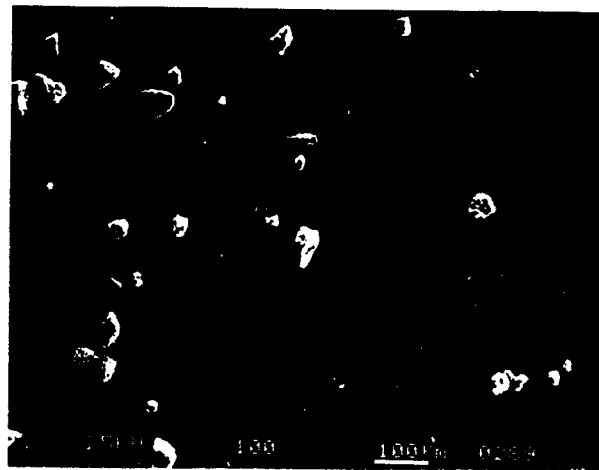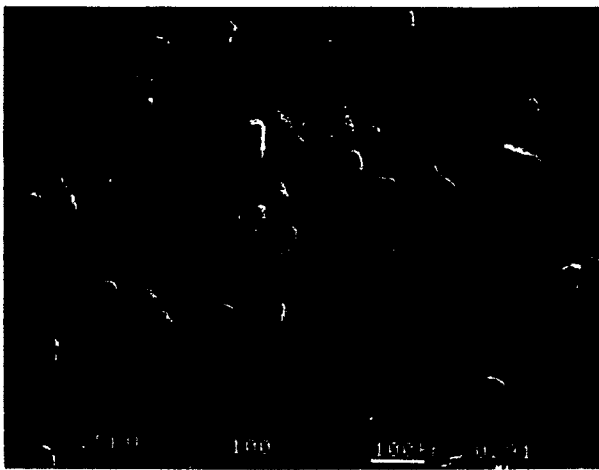
Micrographs D1; Zero Minutes; Largest Size and Characteristic Size

100 micron

Micrograph D2; 0.5 Minutes;

Figure 5 A SEM Micrographs of Decantation Slides Before T-P Process
at X100.
Showing the effect of settling time on the size of the particles
remaining in suspension. The particle agglomerates have a
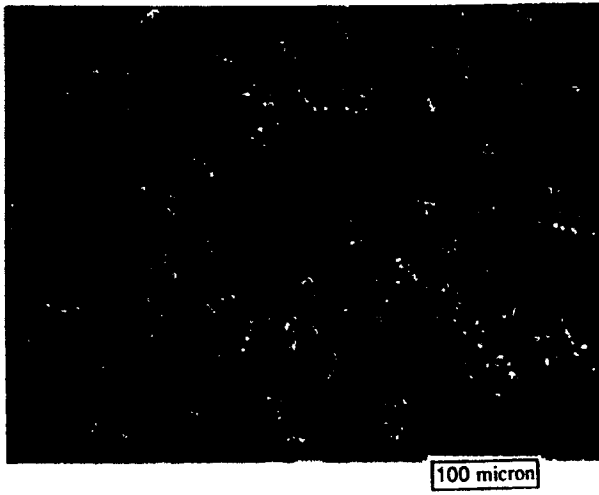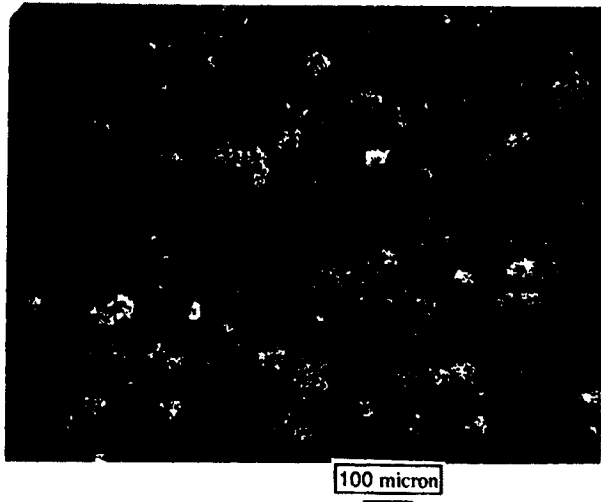pronounced 3rd dimension.

Micrograph D3; 1.5 Minutes;

Micrograph D4; 3.5 Minutes

Figure 5 B SEM Micrographs of Decantation Slides Before T-P Process at X100. Showing the effect of settling time on the size of the particles remaining in suspension. The micrographs reveal that the large sized (60-100 μm) particles settle in ~ 2 minutes.

Micrographs D11; 0.5 Minutes; Largest Size and Characteristic Size

Micrograph D12; 1.5 Minutes;

Micrograph D13; 2.5 Minutes

Figure 5 C SEM Micrographs of Decantation Slides After T-P Process at
X100.
Showing the effect of settling time on the size of the particles
remaining in suspension. The particle agglomerates are
predominantly planar.

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Micrograph D14; 4.5 Minutes; Largest Size and Characteristic Size
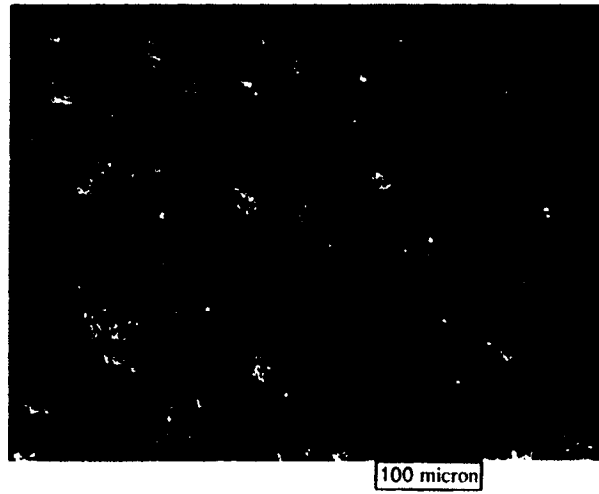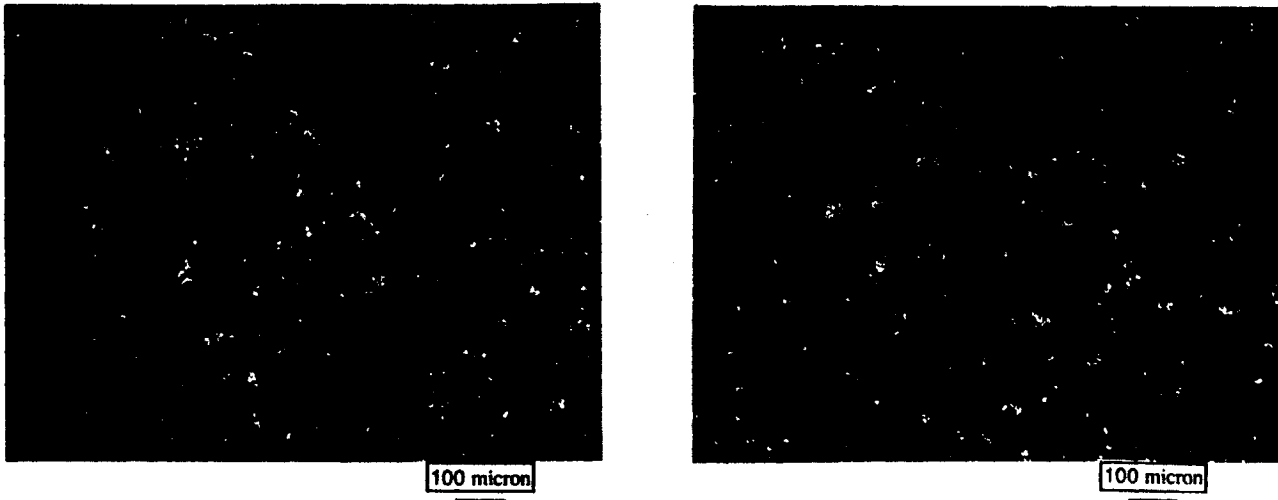

Micrograph D15; 6.5 Minutes

Figure 5 D SEM Micrographs of Decantation Slides After T-P Process at
X100.
Showing the effect of settling time on the size of the particles
remaining in suspension. The micrographs show that 4 to 6
minutes, is, on the average, a reasonable time for settling the
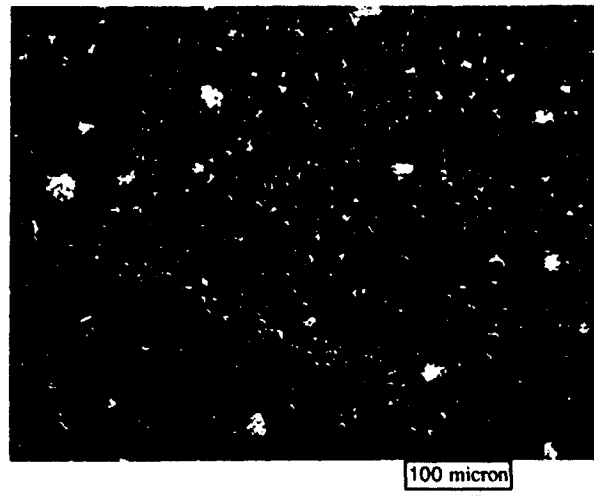tungsten carbide and cobalt, larger agglomerates.

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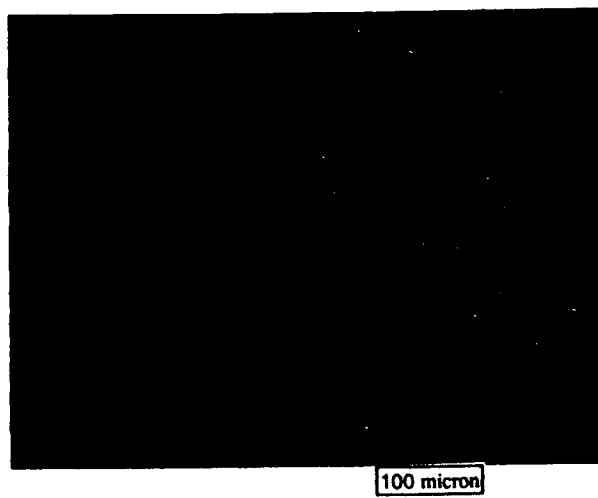
Decantation Time 10.5 minutes

Figure 5 E SEM Micrographs of Decantation Slides After T-P Process at
X100.
Showing the effect of settling time on the size of the particles
remaining in suspension. The micrographs show that after
~10 minutes, all large agglomerates have settled.

in the micron to sub-micron range while the centrifugal forces only settle particles that are agglomerated (both diamond and impurity agglomerates). The supernatant fluid is also found to contain diamond aggregates, although these are small compared to those found in the settled part. The results of the tests with filtrate are given in Table IV. The settled part and the supernatant fluid were observed in an optical microscope at X100 and X400 to observe the distribution of aggregates and individual particles. A 2.7 μm filter paper was used and each centrifuging was carried out for 3 minutes. Centrifuging the filtrate was carried out because of very few impurities present in the filtrate compared to the decantant. The process is an effective way of concentrating the filtrate.

Experiments with Filtration process

Effect of Size of Filter Paper on Yield : To investigate the effect of surface area of the filter element on yield, the following experiments were conducted: A 5 cm diameter, a 11 cm diameter paper cut to half size, and a 11 cm diameter filter paper were used. The results obtained are shown in Figure 6. It can be concluded that the effect of an increase in the size of the filter paper is an increase in the yield. The slope of the graph shows this effect. As soon as the filter element is changed from a 5 cm filter to a 11 cm filter, the slope changes considerably. This indicates that if the filter paper does not get clogged, the yield will be high. As the filtration proceeds further, the yield decreases because the amount of pulverized sludge being treated decreases with every decantation.

Effect of Filter Paper Size and T-P Treatment on Rate of Filtration : The aim here is to investigate the effect of concentration of the suspension (and thus the volume of decantant that may be effectively filtered) for a given area of filter paper. If the filter paper gets clogged, the possibility of diamond particles getting trapped on the filter paper would increase. Hence, for best use of the filter paper and effective filtration, the volume that can be filtered was found. Although the data collected has an inherent variation (as the concentration of the solution differs each time), it reveals useful trends and

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TABLE IV

OPTICAL MICROSCOPE ANALYSIS OF FILTRATE

Video Frame Number, Slide Number, Type	Magnification, Centrifuging Rpm	Observations at X100 Magnification	Observations at X400 Magnification	Comments
1, DC1, Supernatant fluid 01, DC1, Settled part	X100 and X400, 200 X100 and X400, 200	Diamond aggregates observed Diamond aggregates observed	Few comparatively smaller aggregates are observed. Diamond particles are found mixed with impurities.	The supernatant fluid and the settled part both show diamond. The supernatant part shows small aggregates, or rarely, individual diamonds. The settled part has much larger agglomerates and these are usually found surrounded with impurities.
2, DC2, Supernatant fluid 02, DC1, Settled part	X100 and X400, 400 X100 and X400, 400	Diamond aggregates observed Diamond aggregates observed	Few comparatively smaller aggregates are observed. Diamond particles are found mixed with impurities.	No notable change is observed diamond particle aggregate size and individual size.
3, DC3, Supernatant fluid 03, DC3, Settled part	X100 and X400, 800 X100 and X400, 800	Diamond aggregates observed Diamond aggregates observed	Few comparatively smaller aggregates are observed. Lesser impurities are found. Diamond particles are found mixed with impurities	Chained agglomeration is some times observed at the edges of the drops. The quantity and the size of aggregates is not significantly different from the previous centrifuging results.
4, DC4, Supernatant fluid 04, DC4, Settled part	100 and X400, 3200 X100 and X400, 3200	Diamond aggregates observed Diamond aggregates observed	Few comparatively smaller aggregates are observed. Lesser impurities are found. Diamond particles are found mixed with impurities	Both supernatant fluid and settled part reveal diamond and diamond aggregates. Although the supernatant fluid has considerably less impurities, the settled part is not significantly different from the experiments using 200 rpm centrifuging.

facilitates in the understanding of the filtration process. Each set of data in Figure 7 is for a similar experimental condition. Set I and Set II are referred to, as the filtration data obtained before and after T-P treatment respectively. Progressive clogging is characteristic of the former due to comparatively larger particles present. These larger aggregates tend to block the pores of the filter paper by covering it up. In the latter case, although filtration is slower due to increased concentration of fines, clogging is comparatively slower (since larger particles are present in smaller numbers). Set III corresponds a decrease in the concentration of fine particles and lower decantation times have been used to collect larger aggregates of diamond. Set IV shows the effect of T-P treatment along with the fact that the number of fines present are not as high as in the Set II. Although progressive clogging is evident, the total volume that is effectively filtered (less than 40 seconds for each 100 ml) is increased, showing that the concentration involved is more favorable. The half area filtration tests are noted in Set V. These indicate that to start with, for filtration of 100 ml, 35 to 40 seconds are required. This is used as a criterion to decide if the filter is effective. When an 11 cm diameter paper is clogged so that it is only 50% effective, it behaves like the half area filter. Table V summarizes the data in these filtration. Following conclusions may be drawn from the above observation table and the filtration plots:

1. In Set I 30 to 50% of the points lie within the 20 second mark indicating that considerable filtration takes place in that time duration range.

2. In Set I 60 to 70% of the points lie within the 40 second mark indicating that most of the filtration takes place in that time duration range. Above this mark, 50% or more of the filter does not function effectively (behaves like the half area filtration tests where it takes 35-40 seconds for first 100 ml to filter)

3. After the T-P process, as in the Set II the number of points below the 20 second mark decrease significantly, indicating that large amount of fines are produced (most of the filtration takes place through larger pores as the smaller ones get clogged fast). This is the case in spite of 100% dilution. The number of points

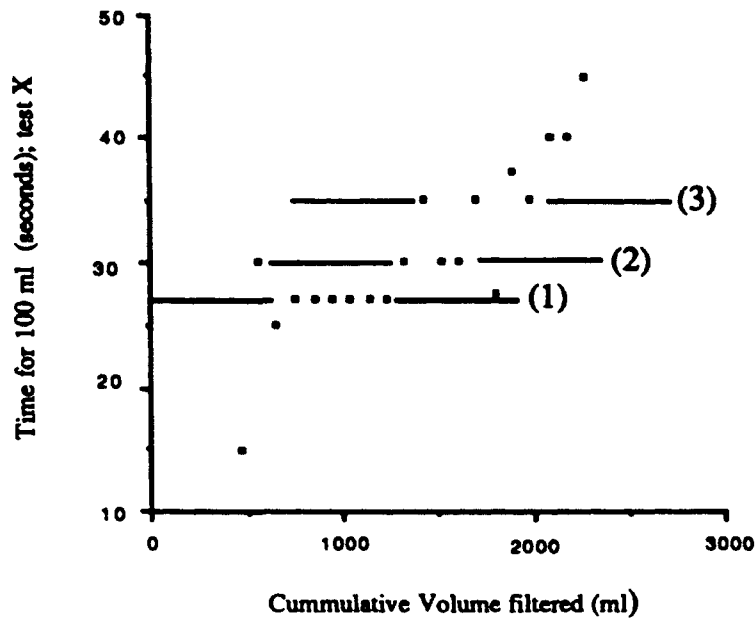Figure 7 A Tests carried out After the T-P Process (from
filtration tests, Set II).
Plot shows equal times for the filtration of ~100 ml
of the filtrate for 2 to 5 successive experimental data
points along lines 1, 2, 3 respectively.
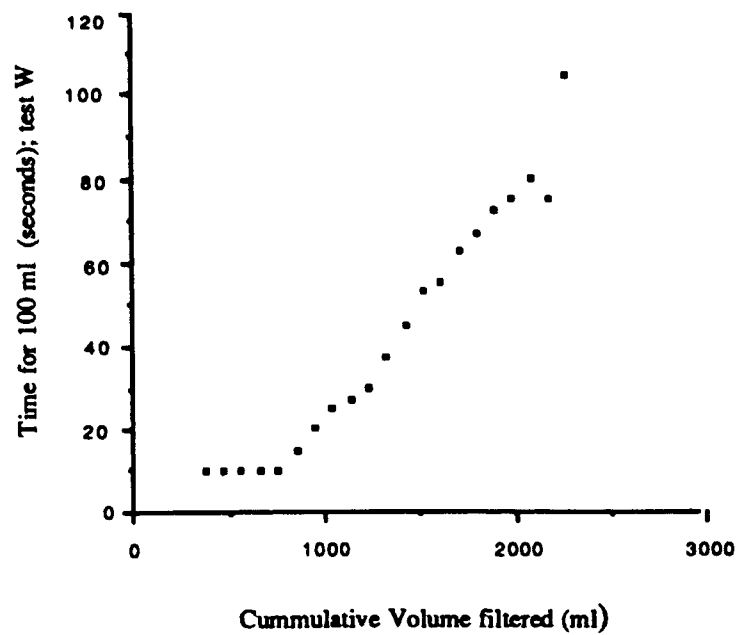
Figure 7 B Tests carried out Before T-P Process (from
filtration tests, Set I).
Plot shows typical progressive clogging of the
filter paper after the initial ~300 ml of filtration.

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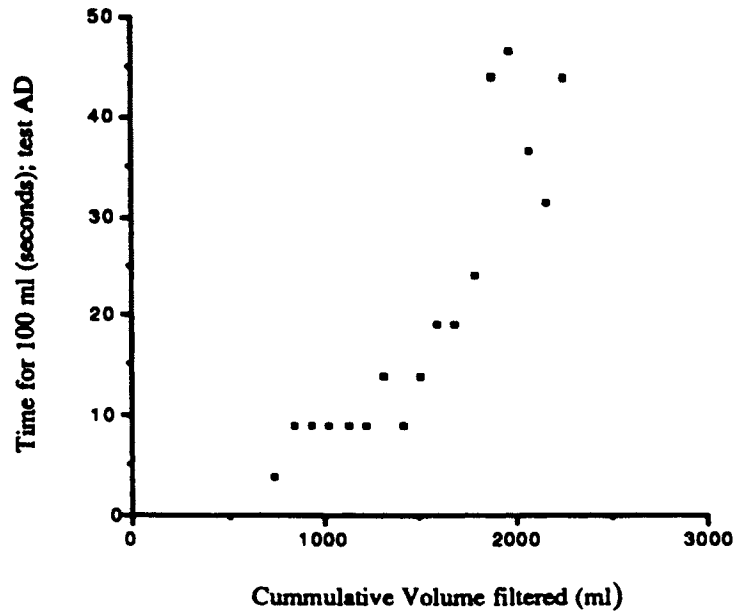
Figure 7 C Tests carried out After T-P Process and After the Experiments in Set II (from filtration tests, set III).
Plots show low threshold time (time required for the first 100 ml to be filtered). The presence of fine particles (due to presence of experimental points with equal times) and dilute solution (low threshold time) is indicated by the plot.
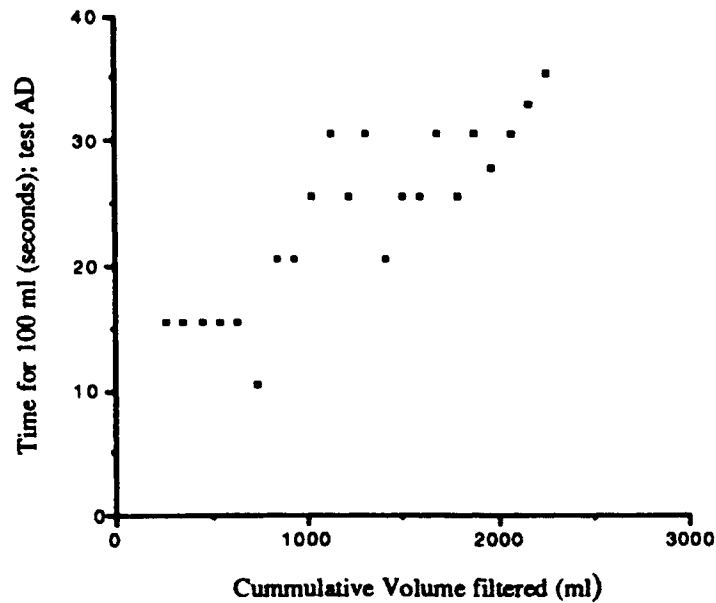
Figure 7 D Tests carried out After 2nd T-P Process (from filtration tests, set IV).
The number of fine particles have increased as compared to previous case. Threshold time is ~15 seconds indicating lesser number of fine particles as compared to Set II.

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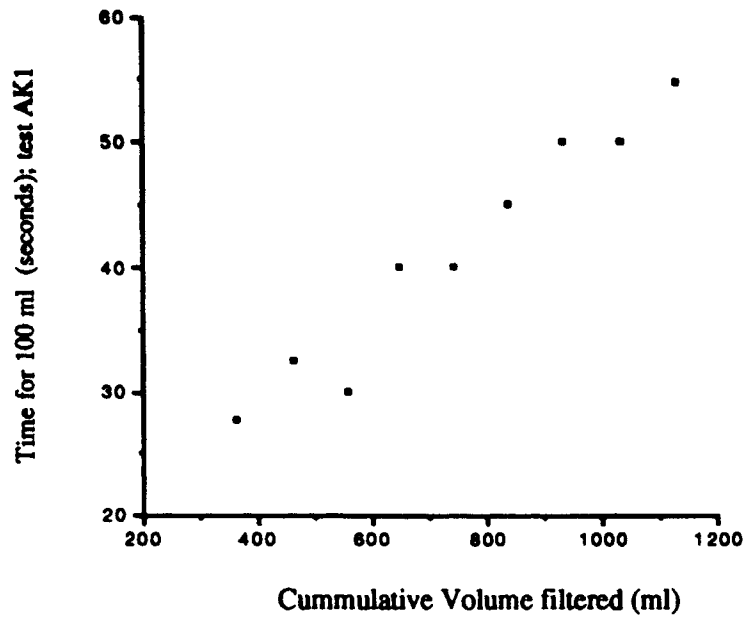
Figure 7 E   Half Area Filtration Tests (from filtration
tests, set V) .
The concentration of fine and coarse particles
is high for the area used and threshold time
is found to increase to 30 seconds.
Progressive clogging is also observed.

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TABLE V

FILTRATION DATA FOR ILLUSTRATING THE EFFECT OF T-P TREATMENT
AND FOR OBTAINING THE OPTIMUM VOLUME THAT
MAY BE FILTERED

Set Number	Plot Label	No. of Data Points Below the 20 Seconds Mark	No. of Data Points Below the 40 Seconds Mark	Total Number of Data Points	Cumulative Volume (every 100 ml filtered in <=40 seconds)
	T	10	14	21	1700
	U	10	13	18	1400
Set I	V	8	13	20	1200
	W	7	11	21	1500
	X*	1	17	20	1500
Set II	Y	3	20	20	1700
	Z	2	17	20	1600
	AA	4	12	19	1500
	AB	10	19	20	1700
Set III	AC	7	18	22	2000
	AD	9	14	17	1500
	AF	14	19	21	1700

TABLE V (Continued)

FILTRATION DATA FOR ILLUSTRATING THE EFFECT OF T-P TREATMENT
AND FOR OBTAINING THE OPTIMUM VOLUME THAT
MAY BE FILTERED

Set Number	Plot Label	No. of Data Points Below the 20 Seconds Mark	No. of Data Points Below the 40 Seconds Mark	Total Number of Data Points	Cumulative Volume (every 100 ml filtered in <=40 seconds)
Set IV	AG*	6	21	21	2300
	AI	7	21	21	2300
	AJ2	0 (1 below 30)	5	8	500
Set V	AK1	0 (1 below 30)	5	9	500
	AK2	0 (0 below 30)	4	9	400
	AL2	1 (2 below 30)	4	9	400

below the 40 seconds mark is significantly altered (85-100% of the points lie in this range). This may be due to dilution.

4. After 4 decantations, the number of points below the 20 seconds mark increases. The number of points below the 40 second mark also increases significantly as compared to Set I. This may be due to a dwindling number of fines in the decantant suggesting that T-P treatment may be required.

Effect of Flocculants on Filtrate: Different flocculants such as ammonium sulfate, magnesium sulfate, and aluminium potassium sulfate were used in small quantities in an attempt to coagulate small aggregates of diamond particles that are suspended in the filtrate. This was carried out with an intention of concentrating the filtrate faster than concentrating it by boiling off the water. The observations are summarized in Table VI. It can be concluded from these experiments that aluminium potassium sulfate (alum) is an effective flocculating reagent. The disadvantage being, it will find its way into the diamond powder and make it impure.

Effect of Time (Number of Filtrations) on the Yield after each T-P process: After the T-P treatment there is a rise in the yield observed. When successive filtrations are continued the yield falls. Figure 8 shows the effect of time on yield after a T-P process. It can be concluded from the figure that after a certain number of filtrations the T-P treatment is required for effective recovery. Usually 3 to 6 filtrations are found to be satisfactory after which the T-P treatment has to be carried out. Although it may be ideal to carry out the T-P process every time from the point of view of effective release diamond particles, the filtration process will not be effective since the number of fines will be very high.

Effect of Pore Size on Yield

The filter paper used initially has a retention rating above 2.7 μm. This has been found suitable for the purpose of experimentation because it does not allow larger particles to pass through, resulting in a good quality filtrate. When 2 to 5 μm filter was used, the

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TABLE VI

EFFECT OF FLOCCULANTS ON FILTRATE

Flocculant	Details of Experiment	Comments and Observations
Ammonium Sulfate	1 gram; Settling time : 10 minutes; 50 ml filtrated was used	No effect was observed. When a sample from the top of the filtrate was examined, diamond particles were found to be present.
Magnesium Sulfate	1 gram; Settling time : 10 minutes; 50 ml filtrated was used	No effect was observed. When a sample from the top of the filtrate was examined, diamonds were found to be present.
Aluminium Potassium Sulfate	1 gram; Settling time : 10 minutes; 50 ml filtrated was used. Observations were made with the help of optical microscope.	Coagulation results in 10 minutes. The precipitate has considerable diamond particles coagulated and in the form of small aggregates, proving coagulation is caused by reagent. Coagulation results in small aggregates of diamond particles indicating that the concentration of the filtrate is not high.
Prolonged Heating	Heating till 80% of water evaporates. 500 ml of filtrate was used. Heated for 1 hour	Thick sediments begin to appear due to concentration of filtrate. These sediments when observed in the optical microscope, appear as lumps formed due to coagulation of large number of smaller aggregates or individual diamonds.

diamond powder collected was found to be of inconsistent quality. Some cases showed considerable amount of impurities in the diamond powder.

Effect of T-P Process on Yield

It can be seen that the yield is significantly affected by the T-P process. Figure 9 shows the effect of T-P process on yield. There are other factors which may also be responsible for increased yield. These include faulty filter gasket, increased filter area, pore size of the filter, and concentration of the decantant. The increase in the yield of diamond powder due to increase in the impurities that weigh much more than the diamond (S.G. is 3 to 5 times that of diamond) is an important issue that must be considered while quantifying the yield.

Optical Microscope and SEM Analysis of the Standard and Recovered Diamond Powder

To qualitatively compare the commercial diamond powders an optical microscope was used. It not only reveals the condition of the diamond in the powder i.e., whether diamonds appear as aggregates or appears singly but also gives an estimate of the quantity of impurities present. When the diamonds are relatively large, it reveals the size and, variation, and shape. It can also reveal whether the powder contains one or more impurities since, different elements reflect different colors.

When observed in an optical microscope, the recovered diamond powder appears very similar to the standard diamond powders for the same range of particle size. The comparison of observations for standard diamond powder is given in Table VII. It can be concluded that the diamond powder contains irregular shapes and mixed with impurities. As the size of the diamond powder decreases, the impurities present are found to increase. The shape of the diamond particles present in the diamond powder depends on the process used in the manufacture of diamond and the comminution process used. If the diamonds are grown to a specific size range, they would appear to have well defined geometrical
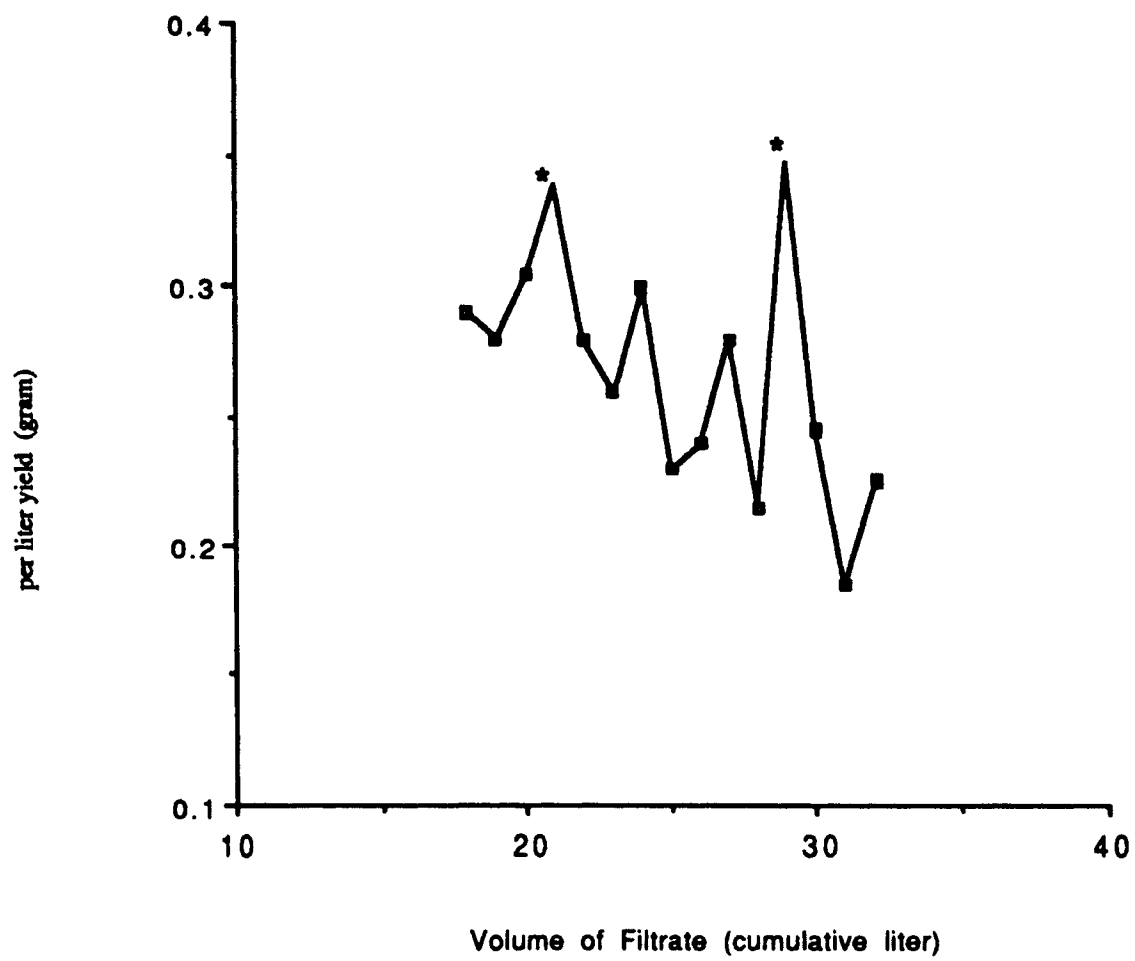
Figure 8 Effect of the Number of Filtrations on Yield After a T-P Process.
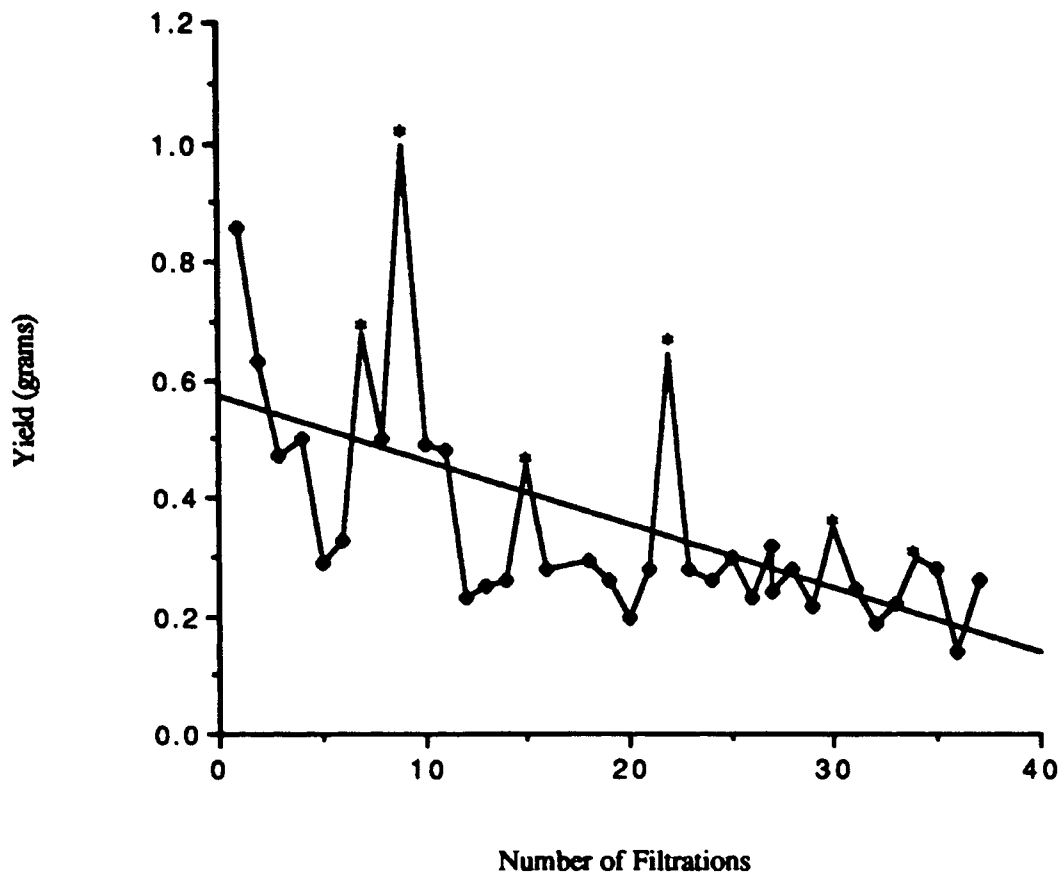Plot shows the diminishing yield after a T-P process.

Figure 9 Effect of the T-P Process on Yield.
The T-P process increases the yield of the diamond recovery process. The effectiveness diminishes with the number of filtrations.

shapes. But if they are made by crushing larger diamonds, they would not have uniform shape. All the diamond powders observed, including the recovered diamond particles, appear to fall in the latter category. These observations are summarized in the Table VII.

When a standard 1 μm sample (14 in Table VII) was observed under the SEM, it appears as small aggregates. The micrographs in Figure 10 A show the sample at 3 different magnifications namely, X100, X500, X1050. This sample was ultrasonically cleaned. Aggregates of 5 to 10 μm were observed. These were found to be separated from each other, as may be observed in the X100 micrograph, although some aggregation to form larger lumps may also be observed. When the standard 6 μm sample was observed, the micrographs obtained revealed the shape of individual particles. These are shown in Figure 10 B. Observations of the reclaimed diamond powder are noted in the Table VII, and the micrographs are given in Figure 10 C. The micrographs reveal that the powder largely contains aggregates of diamonds.

TABLE VII

COMPARISON OF DIAMOND POWDERS USING OPTICAL MICROSCOPE

Video Frame Number	Nominal Size of Diamond and type	Observations at X100	Observations at X400	Comments
10	1 μm Buehler colloidal diamond spray	Appears as bright agglomerates of fine particles	Individual diamonds are not observed, although smaller aggregates are be observed	The suspending fluid may be responsible for the agglomeration.
11	3 μm Buehler colloidal diamond spray	Appears as individual as well as aggregates	Individual diamonds are observed	The diamonds are observed to be very irregularly shaped
12	0.25 μm Buehler colloidal diamond spray	Appears as black aggregates	Appears as bright aggregates	No individual diamonds are observed
13	0.25 μm Norton diamond powder	Appears as black aggregate	Appears as bright aggregates with black impurities	In spite of ultrasonic cleaning using methyl alcohol for 10 minutes, the diamonds are rarely observed as individual particles

TABLE VII (Continued)

COMPARISON OF DIAMOND POWDERS USING OPTICAL MICROSCOPE

Video Frame Number	Nominal Size of diamond and type	Observations at X100	Observations at X400	Comments
14	1 μm ITI diamond powder	Appears as bright aggregates	Rarely individual diamonds are observed	In spite of ultrasonic cleaning using trichloroethylene, for 10 minutes, the diamonds are rarely observed as individual particles
15	6 μm diamond	Appear as dull irregularly shaped individuals	Appear as irregular and individual particles	No agglomeration is observed
16	Recovered Diamond Powered	Appears as bright aggregates	Appears as aggreagates of irregular particles with bright yellow hue	In spite of ultrasonic cleaning using trichloroethylene, for 10 minutes, the diamonds are rarely observed as individual particles

CHAPTER 5

DISCUSSION

Discussion on Centrifuging, Decantation, Filtration, and Distillation Processes.

Centrifuging Process: When a centrifuging process was used to separate the diamond and heavier constituents of the sludge, a thick layer at the bottom containing all the sludge elements was formed. It may be caused by the degradation of oil due to the heat generated during centrifuging.

The centrifuging method employed in the present experimental work did not result in an effective separation of diamonds from the filtrate. In all likelihood, diamond particles may have cleaved during polishing, due to the polishing pressures and long term usage, exposing fresh diamond surfaces. The latter readily adsorb oil film and form colloids in oil in water. Because of this, the centrifuging process did not succeed in separating diamond particles as the particles are held firmly by a liquid dipole.

Decantation Process: The decantation process aims to float the diamonds and separate them from heavier particles. Stirring is carried out before the decantation process to ensure that the diamonds that are loosened from the surrounding sludge constituents are floated. Stirring is found to be critical after the T-P process in order to release the loose diamond from the other constituents of the sludge.

After the T-P process, the mixture was allowed to settle. At this stage the number of fines released is very high. Sufficient time needs to be allowed to settle the diamonds that are >=3 µm. Using Stokes law:

$$\text{Weight of particle in liquid} = 6\,\pi \left(\frac{D}{2}\right)\eta V$$

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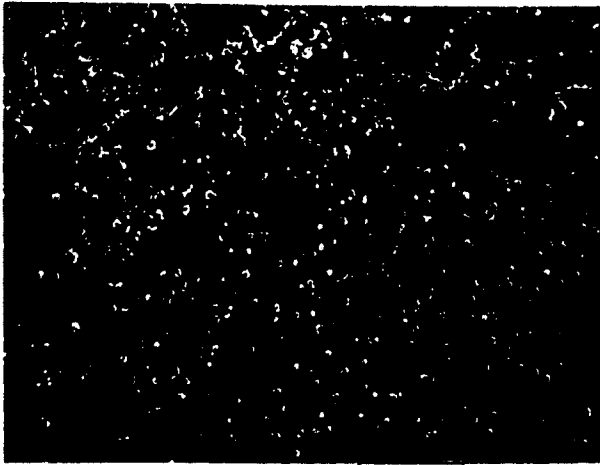
Magnification X100
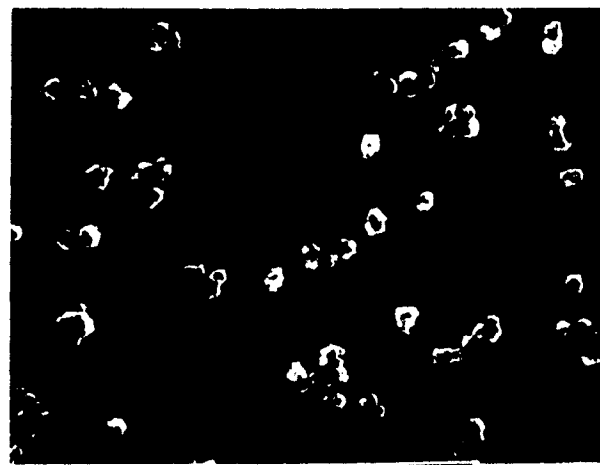
Magnification X400
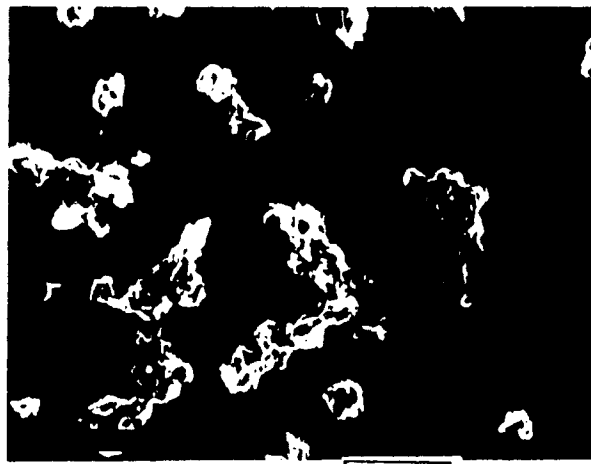
Magnification X1000

Figure 10 A SEM Micrographs of 1 μm Diamond Powder

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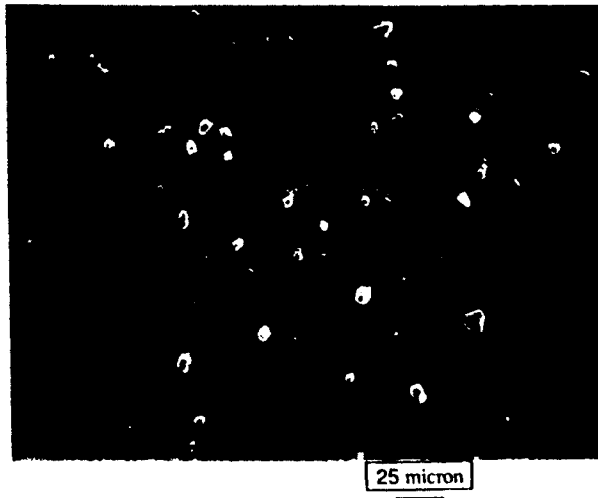
Magnification X400
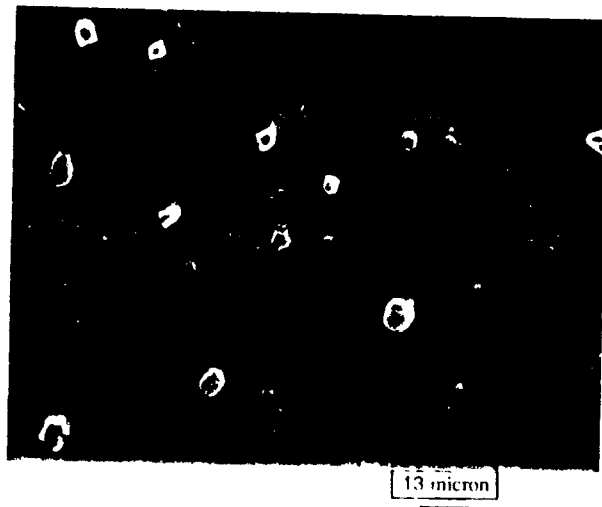
Magnification X750

Figure 10 B SEM Micrographs of 6 μm Diamond Powder
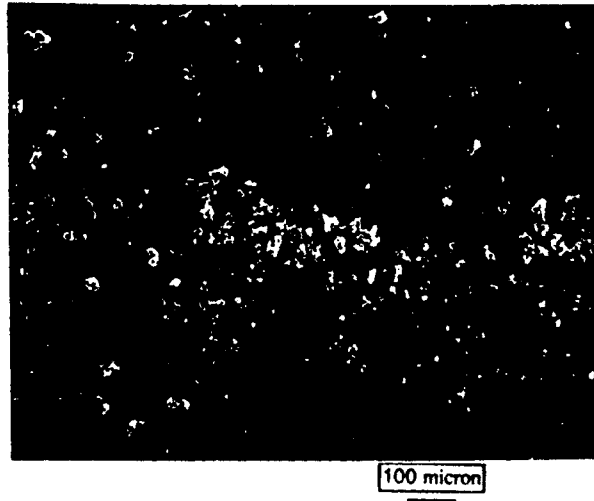
72

Magnification X100

Figure 10 C SEM Micrographs of Reclaimed Diamond
Powder

100 micron
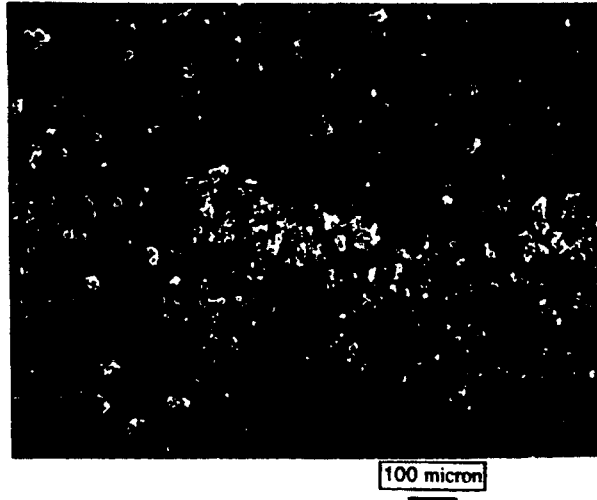
Magnification X100

Figure 10 C SEM Micrographs of Reclaimed Diamond
Powder

Where

D is the diameter of the particle

η is the absolute viscosity of the suspending fluid

V is the velocity of the particles

It is found that in 6 minutes, the diamond particles can travel ~45 mm while cobalt and tungsten carbide particles travel the same distance in 2 and 1 minutes respectively. When decantation is performed, the size of cobalt and tungsten carbide particles is found to be 1.5 μm and 1.2 μm respectively. When <= 2 μm diamond particles are of interest, in 10 minutes, the top 5 mm of the liquid may be decanted and it will contain 0.98 and 1.2 μm particles of tungsten carbide and cobalt respectively. Since there is no significant difference between the size of the unwanted particles in these two cases, the time interval of six minutes was used.

Before the T-P process, larger particles are present in the top layer as the settling time is reduced to 1 to 2 minutes. It is intended to pick up larger agglomerates of diamond in these decantations. The concentrations of fines is very low in these decantations hence the solution is clearer and can be handled more easily. In this case, the larger pores of filter paper are expected to let the diamond agglomerates pass through while holding the relatively large impurity agglomerates. Thus, the membrane filter of 3 μm size was found to be effective for this purpose as opposed to the 2.7 μm filter paper in the former case.

Filtration Process: The filtration process aims at separating not only the larger particles of unwanted material that may be present in the decantant, but also the smaller particles due to the low vacuum (15 to 20 mm of Hg) employed. Slow filtration was preferred since it will keep the kinetic energy of the impurity particles sufficiently low so that they tend to stay on the filter paper. When positive pressure filtration was used, it was found that the impurities in the diamond powder increase. This was inferred from the fact, that 100 ml of filtrate from the primary filtration (using filters of size >= 1 μm) resulted in a gray-brown residue from the positive pressure process and a white-brown residue from

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the negative pressure process. The positive filtration process was very useful in the subsequent secondary filtration using very fine filters (0.2 μm).

Insight into the filtration process was gained by studying the rate of the filtration process versus time for each 100 ml of the filtrate plots (Figure 7). The concentration of the fine and the coarse particles, and how their relative presence affected the filtration process can be noted from these plots. The effect of the T-P process was also evident from these plots. The plots included are representatives of each set, all of which are included in Appendix III.

For water to pass through the fine holes of the filter paper, pressure difference is maintained across the filter element. Pressure is used to overcome the capillary resistance and to provide kinetic energy to the fluid. The magnitude of the resistance can be gauged from the following calculations.

The pressure difference used was 20 mm of Hg. Assuming no capillary action and applying Bernoulli's equation, this pressure difference should result in a velocity of 11.5 m/s. But due to capillary resistance, which the pressure energy needs to overcome, the filtration velocities are found to be very low (of the order of few cm/s). Assuming that 10% of the area takes part in filtration (the rest is assumed to be clogged; this being a rather pessimistic estimate), velocity obtained is 0.48 m/s, which is 2 order of magnitudes lower than the calculated velocity. This demonstrates the effect of capillary resistance (when a larger area is considered, say 90% of the filter area, the velocity using experimental data is found to be 0.052 m/s).

The observations in the filtration experiments are described here. Filter paper behaves differently as the relative concentration of fine (3 μm and less) and coarse (3 μm and above) vary. First the observations from Set II are dealt with followed by those from Set I. Observations from Set III and IV are then discussed followed by those in Set V Figure 7 may be referred for typical plots of these sets of observations.

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Figure 7A (from Set II) shows two distinct features. First, several group of points (each consisting of 3 to 8 points) are seen to lie parallel to the X axis, and secondly, there is a step (in the positive direction of Y axis) observed after a set of such points. Further, there are very few points present below the 20 seconds mark. These observations and possible explanations are discussed here.

Fine particles are present in the solution after the T-P treatment (Figure 7A from Set II). Filter paper has a distribution on its pore size. The finest pores of the filter paper are blocked almost immediately, due to the large concentration of fine particles, while the larger pores remain open. This explains very few points observed (1 to 2) below the 20 second mark. Above the 20 second mark, filtration is observed. The fine particles may build up on the margins of a pore. But, due to enough small particles passing through the pores, it remains open either by dislodging the accumulated particles and opening the passage again or by never allowing a build up to occur because of a continuous passage of mixture of solid particles and water. A dynamic equilibrium appears to be achieved between the number of pores being temporarily clogged and those that are reopened. This explains the consecutive points at the same value of time for 100 ml of filtrate and also a large number of points below the 40 second mark in this figure. The step, separating two set of points parallel to the X axis, may be due to irreversible clogging of some of the pores that were active. This is likely because of the presence of coarse particles. These particles block the active pores irreversibly and result in an increase in filtration time. As the concentration of coarse particles increases, this effect may be expected to be more dominant. As the concentration of the coarse particles increases, the length (number of points, in a group, parallel to the X axis) of these steps decreases. As the volume to be filtered decreases, the concentration of coarse particles on the filter paper increases, thereby reducing the length of these steps. This continues until the stage when the larger and smaller capillaries are progressively clogged and filter paper becomes ineffective.

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When the particles present are predominantly large (~ 3 μm in diameter) and their concentration is low, as is the case before the T-P treatment (Figure 7 B from Set I) due to the low settling times allowed, the filtration process can be explained as follows: due to very low concentration of fine particles (these having been removed in several decantations following the T-P treatment), the initial clogging of the fine pores on the filter paper does not occur. This may explain the behavior of the filter paper initially, when lower values of time are found to be required for filtering each 100 ml. Soon the larger particles start blocking the smaller pores and steadily decrease the filtration rate. Progressive clogging before the T-P process may be due to this (the equilibrium between the number of pores blocked and those reopened is very seldom reached which explains why no more than 2 points are on the same horizontal line). Steady clogging was very pronounced after an initial 300 to 400 ml of filtration.

In Figure 7 C (from Set III), the case AA is a transition between Set II and Set III, since the number of points below 20 are increasing. Also, as compared to Set I, generally, the number of points below the 40 second mark are more than that in Set III. This may be attributed to a lower concentration of particles. The concentrations in this set are more suitable than those in Set I because of settling times that are closer to 2 minutes.

The Figure 7 D (from Set IV which is also just after the T-P process, similar to Set II) shows that the concentration of fines is less than that in Set II. Numerous steps of equilibrium points are seen when the total area of the active pores is almost constant, as a characteristic of the plot. The number of points below the 40 second mark are higher than those in Set II.

Figure 7 E (from Set V) shows the data from the half area filtration tests which were carried out to find out how the decrease in area affects the filtration process. The plots not only show progressive clogging (although they are a continuation of Set IV), but also a high threshold time for the filtration of the first 100 ml. Very few points were found below the 30 second mark. This is probably due to the increased number of fine particles that are

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needed to block the pores such that progressive clogging starts much earlier. It may therefore be concluded that for a concentration of fines produced in a 2000 ml volume (the volume of water mixed each time), an 11 cm diameter filter paper starts behaving as a half area filter paper after filtering ~1200 ml of decantant. The volume filtered below the 40 second mark is reduced with a decrease in the size of the filter paper area (from ~1400 ml on the average to 450 ml on the average)

Distillation Process : This process was used to concentrate the filtrate in order to obtain diamond powder. A stirrer rotating at high speed (1500 rpm) was used to keep the boiling filtrate in motion. This was expected to facilitate the nucleation of coagulated particles. Once large aggregates were formed in sufficient numbers, their presence was likely to hasten a further coagulation process. When larger aggregates were formed in a sufficiently large number, the rpm was reduced to 200 so that the coagulated particles would not shear and fall apart. This was usually delayed until the volume of the liquid was reduced from 2000 to 500 ml. Slow stirring also ensured that no diamonds settle at the bottom of the boiler.

Although initially distillation was used only for the purpose of concentration, it was later replaced by the combination of distillation and secondary filtration. The filtration was carried out when the volume of the concentrate was 500 to 600 ml. To further hasten the process of concentration, flocculants in low concentrations (0.1 % by weight of solution) were added. Alum was found to be a good flocculant and the flocculation process was positively affected by using high speed stirring after mixing the reagent. Membrane filters (0.2 μm) were used in the secondary filter were found to be effective.

Significance of the Thermal Treatment Process

The objective of the thermal treatment process was to remove all traces of oil. The objective of the T-P process was to ensure the release of diamonds from the tungsten carbide-cobalt mixture. The surfaces of the powdered sludge previously unexposed to sufficient heat (due to uneven heating or inappropriate stirring), were exposed and the

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traces of oil that had not been removed, by previous treatment (Figure 1) were removed by evaporation. The reason for carrying out the thermal treatment before the T-P treatment was to ensure that no traces of oil remained when the T-P treatment was being carried out for even a small quantity of oil was enough to initiate a fire when the pulverized sludge was heated to ~450 °C during the T-P treatment. The possibility of oil accidently passing into the powdered sludge, as obtained from the in Figure 2, cannot be ruled out. In fact, the powdered sludge usually was stored and handled before it was subjected to the diamond recovery process. The amount of powdered sludge produced after the oil recovery was many times more (approximately 800 grams of dry sludge resulted from the treatment of 1 liter of the as received sludge, as against only 100 grams were treated at a time for diamond recovery) than what could be subjected to the diamond recovery process which storage necessary and increased the chances of contamination of the powdered sludge. The thermal treatment was carried out just once for a batch of powdered sludge (100 gram), while the T-P treatment was used many times in order to ensure the release of diamonds.

Since the oil present in the as received sludge holds all the elements (diamond, tungsten carbide and cobalt), it needs to be removed completely before any effective diamond recovery may be considered. Hence the thermal treatment process is a prerequisite to the T-P process. Care was taken to ensure that oil did not ignite (since the operating temperature was close to the flash point of oil). If the oil catches fire, the fine diamond may be burnt. The risk may be reduced by using a furnace filled with inert gas or by having a provision for the evacuation of the furnace.

Significance of the T-P process

The process was found to increase the yield and improve the filtration by increasing the number of diamonds released and by letting them pass through the filter paper more effectively. The effect of the T-P process on the yield is illustrated in Figure 9. For a given amount of powdered sludge, the T-P process was initially more effective. The figure shows the decreasing trend not only in the yield in general, but also in the yield after the T-

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P processes. This may be due to the decrease in number of diamonds in the sludge, with each filtration process. Hence, after a particular time it is better to stop treating the sludge, and rather use a fresh batch of sludge for treatment. It may appear that successive T-P treatments are desirable as the yield in between the successive filtrations progressively decreases. However, since the filtration process requires that the concentration be maintained so that the filter paper is effectively used, else more diamonds are likely to be left on the filter paper.

The T-P process was repeated often in the complete treatment of the powdered sludge. The effectiveness of the diamond recovery process depends on the T-P process. If diamond is effectively released during the T-P process, it is possible to separate it in a few decantations. If the process is not effectively carried out, it may have to be repeated (as shown in the B in Figure 2 in the loop shown in the right half).

Observations on Centrifuging the As-Received Sludge

The as-received sludge was subjected to centrifuging in order to reduce the solid content of the sludge. This was required as the distillation process was found to become more efficient when the heavy and fine particles were removed. Experiments were carried out at different rpms to find the optimum rpm for maximum sludge removal.

Observations were noted and they revealed that when the as-received sludge was centrifuged at lower speeds, the heavy fraction of sludge collected was very small. When the slurry was centrifuged at 2500 rpm for 5 minutes, the amount of sludge collected was total of 0.28 kg (from 1000 ml of slurry).

The following calculations reveal the effectiveness of the centrifuging process. The speed of centrifuging was 4000 rpm and period of centrifuging was 5 minutes.

Amount of sludge slurry taken in one centrifuge bottle: 0.82 kg

Amount of sludge that settled, after centrifuging process, in one centrifuging bottle : 0.345 kg

Amount of oil taken by volume in each bottle : 430 ml (S.G. is as 0.94)

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The weight of oil per 500 ml of as received sludge is 0.404 kg. From this, the weight of tungsten carbide-cobalt-diamond powder mixture is 0.416 kg. Since 0.350 kg was found settled, it was concluded that ≈ 0.071 kg or 71 grams of tungsten carbide-cobalt-diamond powder mixture was still present per 500 ml of the centrifuged as received sludge. Some portion of this was separated by subjecting it to a high velocity centrifuging process. The rest was separated in the distillation process, as described above. These experiments show that the centrifuging process is beneficial for the oil recovery process.

Oil Distillation Process

The distillation process, followed in the recovery of oil, is an essential process from several points of view. First of all, the efficiency of the process directly affects the cost of oil recovery. Secondly, the boiling process is sensitive to the boiling conditions and directly affect the success of the distillation process. These points will be elaborated in next few paragraphs. The design of the stirrer used (which is discussed here) is a result of the problems faced during the boiling process.

The boiling phenomenon observed while treating the decantant (from the centrifuged or from the plain decanted sludge), was observed to have the following characteristics:

1) On heating the decantant (after the centrifuging or following the decantation of the as received sludge), within 5-7 minutes (without the whole mass of the sludge reaching a homogeneous temperature), and bubbles of evaporated oil start forming. The bubbles formed are low in number, they tend to be held up in the fluid instead of surfacing and bursting. This is not a suitable condition for efficient boiling process.

2) The bubbles have been found to contain a lot of gas trapped in them. They burst with a characteristic loud noise and the following explosions are strong enough to throw the boiler out of position. For example, when a 100 ml beaker was filled with 30 ml of as received sludge boiling on low heat (on a 200 Watt heater), the bubbles exploded to throw the beaker out of position.

3) When a stirrer was not in use, the inside of the boiler was found to be completely splashed by hot fluid sludge. In such a case, the stirrer bearing is liable to be damaged. Since, the boiling was carried out under vacuum, the splashed fluid found its way into the recovered oil in the collection flask (after passing through the condenser). The oil and the condenser were thus contaminated. Such bursts of bubbles cannot be allowed.

4) The volume of the gas generated was very high and the vacuum (500 to 600 mm of mercury column) was not found to be sufficient. Hence, the rate of heating was controlled. Both, the rate of stirring and heating require close control.

Based on this, it was concluded that the high rate of removal of vapors combined with rapid stirring (speed is limited by the fact that high speed will result in splashing the oil in the boiler) would make the process efficient.

<u>Stirrer Design</u>

Due to the requirements of boiling the decanted sludge (following the decantation or centrifuging route as discussed above), a special stirrer was essential. The stirrer employed had three blades. The lowest (first) was meant to provide a scraping action so that the heavier fraction of the sludge does not settle. It also facilitated the breaking up of the bubbles formed due to evaporation of oil while boiling is in progress. Due to the presence of heavy and fine particle sludge, surrounding the bubbles, a high pressure was developed before the gas could escape. When the gas finally escaped, it had high pressure and the fluid in the top layer being lighter, could not hold it. Thus, the bubbles bursted resulting in splashing. This had immediately clogged the outlet, contaminating the condenser coil and the gasket. The gasket was also damaged since the dried sludge needed to be scraped off.

A middle (second) blade is used to propel the hot fluid layer upwards, so as to mix it with the relatively cooler fluid above. It is mounted at an angle of 90^o (the angle between the longitudinal axes of the two blades, to minimize the effect of the first blade on the other)

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to the first blade, to ensure propelling action. This blade also facilitates the movement of the bubbles to the top.

The top (third) set of blades (two blades) are used to churn (redistribute) the fluid propelled by the second blade. This ensures mixing and homogenization of the fluid temperature. Approximately 75 rpm was found to be suitable for the purpose of stirring satisfactorily under the experimental conditions.

Economics of the Diamond Recovery Process

The thrust of the work here is on developing a physical process of recovery of diamond particles from the sludge and making it technically feasible. The following economic analysis identifies the cost elements involved in the process. Analysis of the variable cost elements is given in the Appendix II, where the process and its variation is discussed. Since the process has been proven on a laboratory scale the analysis is only carried out from this perspective.

The total cost involves the fixed, the labor, and the variable costs. The fixed cost in the diamond recovery process involves the cost of boiler, the condenser, the filter, the five tanks (used one each for quenching, mixing, condensed water collection, and two for decantation purposes), the vacuum pump and the stirrer motor. The vacuum pump and 1/30 Hp A C stirrer motor used, form the major fixed cost components. The filter was made out of 150 mm (5 mm wall thickness) diameter PVC tube. None of these elements require special designing and therefore can be built at a reasonable cost.

The fixed cost in the oil recovery process involves the boiler, the collection tank, the stirrer and the stirrer motor. The stirrer motor is a 1/3 Hp, low speed, high torque (~0.5 N-m) motor. The same vacuum pump and the same condenser, with a separate coil for oil condensation, is used.

The economies of scale, the production methodology, (batch or continuous processing) need to be considered before arriving at reasonable estimates. The cost of

storage, handling, and disposal of the swarf are considerable (upto $1500/ barrel) and also need be considered.

The equipment for the process is simple and needs no specially designed components. However, the filter and the filter element need to be carefully handled and form an important cost element of the recovery system. By careful handling, the life of the secondary filter can be significantly increased.

The variable cost elements are included in the appendix. The analysis is carried out for two variations of the process. First is for the initial process involving the use of the distillation process. The second process replaces the distillation process with a secondary filtration process, that is used in conjunction with the flocculation process. The calculations are given for a 2000 ml of filtrate. The returns from the oil, that is recovered using the process, has not been considered since it is likely to be a small quantity. However, the cost of the recovery of oil is considered for completion of the analysis, though it is found to be a small fraction of the costs involved.

CHAPTER 6

CONCLUSIONS

The conclusions drawn from the study conducted are listed as follows:

1. The recovery of fine diamond powder can be achieved by a simple physical processes consisting of pulverization, decantation, filtration, concentration, and thermal treatment. Approximately 19 grams of diamond powder was recovered from 100 grams of powdered sludge, resulting in ~90% recovery by weight of diamond powder present.

2. The recovery of oil, used as a carrier in the polishing process was also achieved by the distillation process. Approximately 700 ml of oil was recovered from 1000 ml of as-received sludge.

3. The centrifuging process when used for the separation of diamond from the polishing sludge is not effective (upto 4000 rpm). Instead, black mass containing all the solids resulted.

4. The efficiency of the recovery of diamond recovery was found to depend on the effective implementation of the thermal treatment-pulverizing process, the decantation process, the filtration process, and the concentration process.

5. The optimum time for decantation, before the thermal treatment-pulverizing process was found to be 1 to 2 minutes, while that after the thermal treatment-pulverizing process was found to be 4 to 6 minutes.

6. When a 2.7 μm (Whatman 42) filter paper was used, the volume that can be effectively filtered was found to be ~1200 ml. This volume increases to 1500 ml when 3 to 4 filtrations are performed.

7. The thermal treatment-pulverizing process was found to affect the yield of diamond powder in the recovery process. For example, it was found that the yield could be increased by ~100% (range observed was 60% to 200%).

8. The frequency of the thermal treatment-pulverizing process can be increased if the area of the filter is sufficiently large.

9. The yield of diamond powder obtained was found to be a function of the filter paper area.

10. Membrane filters were found to be effective for the primary filtration (3 μm) and could be reused after washing gently.

11. Previous methods were not found to be suitable for the separation of fine diamond from the cemented carbide polishing sludge. Moreover, some of them use caustic chemicals.

12. Of the flocculants investigated in the final stages just prior to distillation, namely, magnesium sulfate, ammonium sulfate and aluminium potassium sulfate (alum), the last one was found to be an effective flocculant. Heat has not been found to affect the coagulation process in case of magnesium sulfate, ammonium sulfate and aluminium potassium sulfate.

13. Effect of heat on the coagulation of the small diamond particle aggregates has been found to depend on the concentration of the particles in the solution. Small particles are found to form a thin layer on the top and stick to the distillation vessel. Effect of heat is observed when the concentration gets high (80 to 90% of original volume of filtrate is removed). The coagulation process, was observed mainly towards the end of the distillation process.

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CHAPTER 7

WORK UNDER PROGRESS

Closed Circuit Implementation and Automation Requirements

In this investigation the physical process of diamond recovery from the polishing sludge was demonstrated at a laboratory scale. For implementation of the process on a larger scale, it is necessary to implement the process in a closed circuit to make it continuous. For this purpose, preparation of powdered sludge may be carried out using flash evaporation method. Vacuum may be used to carry fluid in the circuit. In the following a brief account of the work carried out in this direction along with the suggestions based on the experience with the fabricated prototype equipment and the recovery process are given.

Flash evaporation is a technique in which, thoroughly stirred as-received sludge is allowed to fall drop-wise from a specific height through a chamber which is heated externally with the help of a heating element. The heat flux maintained is such that the oil evaporates without igniting by the time the drop reaches the bottom of the tube. This process results in smaller lump of easily crushable material. Both, flash evaporation and distillation processes cannot produce fine particle size without pulverizing. In the case of flash evaporation the falling dry sludge may be carried by a stream of water or a belt conveyer to the pulverizing unit.

A prototype apparatus with a steel tube of 50 mm diameter and 1.3 meters length was used as the furnace chamber. Two heater elements (1500 W each, 11 meters in length

each) were wound on the tube. The tube with the heater elements was covered with a radiation shield. The above assembly was mounted on a vertical column, which in turn was mounted on a base. The base was made of a steel plate held in a frame of slotted angle iron and mounted on wheels. The column was made of slotted angle iron frame. A thermocouple (with temperature range from -190 °C to 1000 °C) was used to measure the temperature in the furnace. It can reach a depth of 0.25 meter in the furnace. Experiments are under way to demonstrate the technical feasibility of the process.

The thermal and pulverizing process unit, the mixing tank, and the decantation tanks may be included in the circuit. The decantation tank may be fitted with a controlled speed propeller to keep it churning the sludge that settles at the bottom of the tank. This would facilitate the release and temporary flotation of diamonds in water. The decantation of the fluid can be carried out when the propeller has been stopped and the liquid has been left standing for suitable time. The fluid can then be fed by the vacuum pump to the filters.

Using two filters in parallel may facilitate reduction of the set up time for filters. While one is being used, the other can be set up. The pleated filter element, which greatly increases the surface area, makes it difficult to reclaim the material held on the filter element. Hence, a pleated element that can be opened up into a sheet after use and washed, may be employed. The primary filter may use a membrane filter while the secondary filter (0.2 μm or less) can either be a membrane filter or a metal filter. The primary filtration may be carried out under negative pressure (0.5 to 0.6 atmospheres) while the secondary filtrations may be carried out under positive pressure (because it is desirable to have minimal impurities in the filtrate after the primary filtration). The filtrate from the secondary filter may be used again in the mixing tank thereby closing the water circuit (although human interventions may be required, the working fluid has completed a cycle).

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APPENDICES

APPENDIX-I

METHODS OF RECOVERY OF DIAMOND FROM ORES AND IMPURITIES

The methods of separation of diamond included here are used for extraction of diamond and for recovery of diamond from polishing sludges other than cemented tungsten carbide sludge. First two methods are used for the extraction of diamond ores. Following methods are discussed.

1. Gravity Concentration
2. Grease Table Separation
3. Electrostatic Separation
4. Electrolytic Separation
5. Magnetic Separation
6. Chemical Separation.

1. Gravity Concentration [8]

This method is used when diamond powder is mixed with impurities that are of different specific gravities in the range of 2.5 to 3.5. Washing pans, or jigs are used for the purpose of concentration. In the case of washing pans, the crushed diamondiferous ore and water mixture is fed into pans. Radial webs stir the mixture, and redistribute the particles along the bed (which is tapered, lower at the center). Diamond is heavier and hence settles at the bottom and towards the center. It can be separated and subjected to further concentration.

Jigs also use water as the working medium. A plunger guided by a cam sets a body of water in a pulsating motion. Crushed diamond ore is placed on a sieve. Water enters

this section of the apparatus from below the sieve. The chamber, where the crushed ore is stored, is filled with pulsating water. The particles separate due to the motion of the water and because of the differences in the specific gravity of the materials involved. The last layer of the powder mixture is largely diamond. This method is repeated several times to get the desired concentration.

The method is simple and well suited for the separation of gem quality diamonds since they settle fast in a suspension of water.

2. Grease Table Separation [8]

An ancient but effective technique uses a slant table, the surface of which is covered with a layer of grease, such as vaseline or petroleum jelly. Slurry consisting of diamondiferous ore is fed at the top end where a uniform flow is maintained. Water not only wets some of the minerals but also rolls the mixture down the table. This method exploits the fact that diamond possesses a greater affinity for grease than for water and is easily wetted by grease. In contrast, other minerals are wetted easily by water and roll down the table with it. This results in the diamond particles sticking to the grease while other mineral particles roll down and are collected as tailings. To ensure minimal loss of diamond in the tailings it is important that the surface of the diamond particles be clean. This can be done by chemical treatment of the powder. Boiling in an alkaline medium such as sodium hydroxide (about 10% by volume) is found to be a satisfactory technique.

An improved technique for separating diamonds uses a grease belt. The diamond swarf is sluiced across the moving grease belt which traps diamonds and carries them to the end where a heated knife scrapes them off. At the other end of the endless belt, fresh grease is applied automatically. The concentrate, with a strong flow of water, is fed across the belt, which is mounted so that it tilts sideways.

This method is also suited for gem sized diamonds that do not have surfaces covered with impurities. The method cannot be used for fine diamond since it tends to flow with water without contacting the grease.

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3. Electrostatic Separation [5-6]

In this process, the separation of diamond is effected by the difference in electrical conductivity of the conducting impurities and the non-conducting diamond. For good results preprocessing of the material may be required for the following reasons:

1. The surface of diamonds may be covered with metal oxides. This makes the surface more conducting. Hence the mixture is subjected to ball milling. Such a process may use 20 steel balls of 25 mm diameter and 50 balls of 19 mm diameter. The resulting powder is washed and deslimed.

2. The surface may be covered with a grease layer. This may render the surface conducting or may help impurities stick to the diamond surface. Cleaning in hot water or even boiling in caustic soda does not help removing the last traces of grease. Boiling the diamond powder in chromic acid assures proper separation.

The method is well suited for coarse sized particles. The loss of diamond due to this method is practically nil unlike the chemical methods.

Rod type Electrostatic Separator: The apparatus consists of a feed hopper which facilitates the distribution of material on a conveyor in a uniform layer. The earthed brass electrode which is 100 mm diameter (for ensuring physical contact between the crushed diamondiferous ore and the electrode, larger surface area is provided), is the one that receives the charge that the separator handles. This charge first passes close to a pin mounted drum, and the particles get charged. These, then fall on a brass roll. On falling on the roll they loose their charge. Since the roll is negatively charged, the impurities, which are positively charged, are attracted to it. The conducting charge gets attracted by the positively charged electrodes resulting in separation.

In an improved separator, the rod electrode is replaced by a rotating roll. This is insulated from earth by placing the shaft bearings in a perspex supports. There is provision for altering the distance between the electrodes. The pin-point electrode is adjustable and can be placed at various distances from the roll electrode thus varying the intensity of the

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ion flow. The brushes are used to keep the surface of the rolls clean from dust. The feed is preheated by infrared element. The intensity of the heat can be changed by raising the temperature.

In case of coarser feeds, the rolls are placed fairly close to enable the relatively weak electro-kinetic forces to deflect the heavy particles more strongly. Typically, for a particle size of 8 mesh the distance is kept less than 25 mm. The parameters that may be changed are rate of feed, speed of roll rotation, and voltage of the rectifier unit. Closer observation of the particle behavior in electrostatic separation indicates the following:

A. High tension laid on stationary electrode only: In this case the conducting particles loose the induced positive charge as soon as they come in contact with the earthed roll. They are therefore attracted by the rod electrode. But diamond being non-conducting retains the induced charge. Hence diamond is attracted by the earthed roll. The separation is thus effected.

The method is not effective for larger diamond size since the charges due to polarization are weak.

B. High tension laid on pin-point electrode only: Owing to the narrow gap between the points and earthed roll surface, (27 mm), ionization of the air causes intense flow of ionized particles between the electrodes. Good conductors describe steeper path as compared with case 'A'. Smaller particles even adhere to the roll and may have to be removed by brush.

C. High tension laid both on the rod electrode and the pin-point electrode: This is the best of the three possible methods described. Here, a strong positively charge is first induced by the pin-point electrode. Diamonds being poor conductors are repelled by both the electrodes. Hence diamonds are deflected to the left. The conducting particles receive strong positive charge but they give it away immediately to the earthed roll. They are repelled from the roll and

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attracted by the positively charged rod. Hence they follow a distinctly different path and clear separation results.

Better separation is noted when the metal electrode is replaced with bakelite electrode. The effect of increasing humidity is observed to be positive. Relative humidity of 54% to 56% is found to be safe.

The method is not suitable for large diamonds, i.e. 4 mm and above, since their weight becomes an over-riding factor. For very small diamonds, i.e. less than a few micrometers, the method is not suitable since the fine diamond particles may be easily held by conducting material that stick to the drum.

4. Electrolytic Separation [3-4]

The method consists of dissolution of the matrix of the diamond containing substances (such as drill crowns, scrap cemented carbide) in a suitable electrolyte. When an additional potential is applied the matrix dissolves anodically. The decomposition of the 'hard' matrix depends on the dissolution of the metallic binding constituents. Electrolytes are used based on the type of material to be dissolved.

A. Bronze Matrices : Different acids and currents are used for different matrices. The following paragraphs describe the different combination and the results.

i) Hydrochloric acid : With 10% solution a maximum of 7 A current was found suitable. The current was found to drop to 0.4 A with the formation of cuprous chloride crust on the matrix. Within 10 minutes all action was found to cease. Hydrochloric acid (20% concentrated) was found to be suitable, but the process resulted in obnoxious fumes.

   i) Hydrochloric acid-Nitric acid : This mixture was rarely found to result in sludge formation but was marked by the liberation of corrosive and poisonous chlorine gas.

   iii) Sulfuric acid: It was marked by sludge formation and evolution of hydrogen.

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iv) Sulfuric Nitric acid: Some sludge and no formation of copper sponge was observed.

v) Nitric acid: Solutions with strength of 15% to 20% were found to give encouraging results. Optimum results were obtained for solutions with 20% strength. This was found to be the most suitable for electro-dissolution of bronze matrices. Nitric acid with hydrofluoboric acid (20% and 1% to 20%) was found to result in no sludge formation.

B. Aluminium-Bronze Matrices: Use of 20% nitric acid was found satisfactory. Matrix was found to be completely decomposed in about 2 hours. No sludge formation was reported.

C. Brass Matrices w/o Iron: Use of 20% Nitric acid was found to be satisfactory. Time required was 1.25 to 1.5 hours. No sludge formation was found to take place.

D. Brass Matrices with Iron: This type of matrices usually contain up to 13% iron, 17 to 22% zinc, 70% copper. Most satisfactory results were obtained when an electrolyte containing a mixture of 20% nitric acid and 10% hydrofluoboric acid was used. This required around 1.5 hours for complete dissolution of the matrix. When 20% nitric acid was used as an electrolyte, 1.7 hours were required for dissolution. No sludge formation was observed.

E. Beryllium-Copper Matrices: Suggested electrolytes in order of preference are as follows:

   i. 20% nitric acid + 10% fluoboric acid : time taken for matrix decomposition was found to be 1 hour and 35 minutes

   ii. 20% nitric acid : time taken for matrix decomposition was found to be 1 hour and 40 minutes

   iii. 5% nitric and 5% sulfuric acid : time taken for matrix decomposition was found to be 1 hour and 50 minutes

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No sludge formation was reported. The electrolyte was continuously agitated while electrolysis was in progress. Current required was found to be ~15 A in all these cases.

F. <u>Monel Metal Matrices</u>: Copper and nickel are present in this alloy in ratio 1: 2. These matrices can be decomposed with 20% nitric acid in ~1 hour and 40 minutes. No sludge was formed and current required was found to be 15 A. With 2.5% sulfuric acid and 5% nitric acid, and using the same current, similar results were obtained. In this case cathode deposit of copper was found to be completely adherent. With electrolyte containing 5% nitric acid and 10% hydrofluoboric acid, the matrix could be decomposed in 2.5 hours and at 10 A. Again copper deposits were found to be firmly adherent to the cathode.

G. <u>Nickel Iron Matrices:</u> This type of matrix consists of 60 to 70% iron with 24 to 34% nickle-tin alloy and 5% nickel. Nickel-tin alloys are very resistant to attack from acid especially due to the presence of iron. Sulfuric acid mixtures do not produce effective results. Complete decomposition of these matrices was achieved by using a mixture of 15% hydrochloric acid and 10% hydrofluoboric acid at a current of 15 A in 1 hour and 40 minutes. When the concentration of hydrofluoboric acid was increased to 20%, time taken was found to be 20 minutes. Hydrochloric acid mixtures proved to be quite effective. With 15% hydrochloric acid such matrices dissolved in 1 hour and 45 minutes at 15 A. The electrolytes remained clear of sludges. A mixture of 20% hydrochloric acid and 20% hydrofluoboric acid was found suitable for two successive dissolutions of EX nickle-iron electrodes.

H. <u>Stainless Steel Matrices</u>: The electrolytic solutions that were found suitable for nickle-iron mixtures were also found suitable for stainless matrices. The time taken was ~ 2 hours.

5. <u>Magnetic Separation</u> [12]

If the swarf contains magnetic material, such as iron or cobalt, magnetic separation should be seriously considered. For this, the swarf is placed in a large porcelain

evaporating dish or flat-bottom glass basin with sufficient carbon tetrachloride or methyl alcohol to cover the solids. A cylindrical magnet ~ 38 mm in diameter is inserted into a 100 ml pyrex beaker. The beaker is stirred around in the wet sample. Magnetic material (cobalt or iron) adheres to the beaker leaving the rest of the powder in the basin. On removing the beaker (along with the magnet) from the basin and withdrawing the magnet the material is released from the exterior of the glass. The procedure is repeated holding the beaker containing the magnet about 6.5 mm above the material in the basin and removing smaller quantities of magnetic material each time. Depending on the size and quantity of the metallic contaminants, this procedure is repeated 3 to 8 times until it is seen that no more magnetic material is left in the basin. The nonmagnetic material is allowed to settle. To separate diamond powder, the liquid is decanted, filtered, distilled and/or centrifuged.

The method is not suited for the polishing sludge in question since it has fine particles in oil. When a magnet is brought near the wall of the beaker containing the sludge, whole mass of the sludge is found to move along with the magnet. On adding trichloroethylene, although cobalt (along with some tungsten carbide and diamond) could be separated, tungsten carbide is not removed by this method and hence the method is not suitable for the problem at hand.

6.Chemical Separation Processes [2, 10, 13-21]

These are based on the type of impurity to be removed from the mixture. The process, in general, requires treatment with acids, alkali, heating processes, and some physical processes for separation such as decantation, centrifuging etc. The removal of following impurities are dealt with :

     A. Removal of grease, oil, fats and other organic matters

     B. Removal of metals

     C. Removal of silica

     D. Removal of cement

     E. Removal of ferrous material

F. Removal of contaminants such as silica, silicates, and alumina

G. Removal of carbide contaminants

H. Removal of glass

I. Removal of graphite

J. Plastic contaminants

A. Removal of Grease, Oil, Fats and Other Organic Matters [13]: Diamond powder is covered with trichloroethylene and heated gently over a flame. After boiling for a few minutes it is removed from the flame. Powder is then allowed to settle. This is followed by decantation of the liquid. Liquid is passed through filter paper (grade Whatman 41) and the residue on the filter paper is washed with trichloroethylene and powder is brushed back in the beaker. After drying, the beaker is gently heated to remove the last traces of trichloethylene. Two or three washings may be required to ensure complete the removal of the material.

B. Removal of Metals [13, 16] : If the diamond particles are between 35 mesh and 325 mesh then the following treatment is given. Approximately 500 ct powder is taken in a 2 liters beaker and 500 ml of chromic acid is added to it. After swirling the mixture to ensure proper mixing, the mixture is heated to 150 °C for 15 minutes with occasional stirring. The diamond powder is allowed to settle for 10 minutes and the supernatant liquid is decanted off. Another 500 ml of hot water is added and the mass stirred then allowed to settle for 10 minutes and the supernatant liquid is decanted.

A mixture of hydrochloric acid and nitric acid (500 ml each) is used to treat 500 ct of diamond powder. The mixture is heated to the boiling point and maintained at that point for 1 hour with constant stirring, after which water was added so as to half-fill the beaker. The mixture is allowed to settle for 10 minutes after which it is decanted.

When the size of the particles is below 325 mesh then powder is treated with 50% solution of nitric acid, and the mixture boiled for 15 minutes. The acid is then diluted with

water and the mixture allowed to settle. The liquid can be either filtered off or decanted. The powder may then be washed with water and dried in an oven.

Dissolution of metallic impurities can be effected by using cold concentrated hydrochloric acid. After the reaction has ceased, the supernatant liquid is decanted and the powder washed and dried.

Another method [16] for cleaning diamond powder, is to treat with a mixture of acids: 20 ml sulfuric acid + 5 ml hydrochloric acid + 5 ml nitric acid + 70 ml water. This mixture (75 to 100 ml) is added to 50 gram of powder. Carbonecious matter should be removed before this process is carried out. To accelerate action, the mixture is heated to 150 °F and stirred intermittently. Dust is allowed to settle and then supernatant fluid poured off and treated powder is washed with the above mixture of acids (10 ml of mixture to 90 ml of water) several times. It is then washed with 30 to 50 ml of water and dried. Finally, dry powder is treated with absolute methyl alcohol and transferred to silica crucible, heated to 800 °C, and stirred while it is being heated. To avoid spattering of the powder due to the presence of moisture, it is heated at a slow rate initially. It is then cooled to room temperature. If powder is not clean enough, for further processing, the process may have to be repeated.

Another method uses hot aqua-regia. This is a satisfactory solvent for metals that contaminate diamond powder. After this treatment the powder is washed several times by decantation and dried in an oven at 120 °C. If the particle size is below 120 mesh, decantation is replaced with centrifuging.

When other impurities are present with metals in diamond powder, it is advisable to carry out initial fusion before treating with aqua-regia. For this purpose the sample is placed in a large iron pot, together with 10 to 15 times its weight of potassium or sodium hydroxide and is fused at a low heat for 15 to 30 minutes. Potassium allows the fusion to be completed faster since it is more reactive. The molten mass is frequently stirred until it develops a light green color. It is then cooled and leached with water and washed several

times by decantation or centrifuging depending on particle size. The mixture is then transferred to a plate and digested with hot aqua-regia, washed several times with water by decantation or centrifuging, and dried in an oven at 120 °C. A second fusion may be necessary followed by acid treatment and washing. It is important to carry out fusion at lowest possible temperatures to prevent the loss of finer diamond particles.

Typical losses are : 10 to 14 mesh fused with potassium hydroxide results in 0.24% loss at a low heat while 200 to 325 mesh under same conditions results in 5.6% loss. Losses with sodium hydroxide are more : 9.5% for 30 minutes for 200 to 325 size powder.

C. Removal of Silica: Diamond powder is washed with hot water (distilled). Then to a 500 ct of washed diamond powder, 10 ml of hydrochloric acid is added. The mixture is shaken to ensure proper mixing. After allowing the mixture to stand for 5 minutes, 500 ml of chromic acid is added. The mixture is heated to 150 to 170 °C and maintained at this range of temperature for 1 hour with intermittent stirring. The mixture is then cooled and 1 liter of water is added. Decantation through filter paper is then commenced. Eight hot water washes of 750 ml each, allowing a few minutes in between the washes, are carried out. This is then washed twice with 250 ml rectified spirit, followed by 250 ml of absolute alcohol.

Another method involves the use of a solution of 10% sulfuric acid and hydrofluoric acid which is added to the diamond powder and the mixture is heated for 1 hour. This removes all traces of silica.

D. Removal of Cement [13]: For this, the powder is taken in cast iron crucible. It is covered with 4 parts of sodium hydroxide and one part of sodium nitrate. It is then heated for about 20 minutes in fused state. The fused mass is dissolved in large excess of water. Powder is allowed to settle down and liquid removed by filtration or decantation. The bulk of powder is washed with hot water followed by dilute hydrochloric acid to remove traces of iron hydroxide.

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E. Removal of Ferrous Material [13]: Before chemical separation of metals is carried out, it is advisable to remove iron by magnetic separation. For this purpose Almico magnet may be used. The magnet is moved over the powder 3 to 4 times to remove possible iron particles.

F. Removal of Contaminants such a (Silica, Silicates, and Alumina) [14, 16, 10]: The sample is placed in a large platinum dish and heated cautiously with hydrofluoric acid. Small amount of sulfuric acid is added until decomposition of the ceramic occurs. It is then washed and decanted with water [14].

If alumina is present [16], the mixture from the above treatment is fused with sodium carbonate in a platinum crucible for ~15 minutes. It is then cooled and leached with water, washed, and acid treated, and dried. Potassium hydroxide may be used instead of sodium carbonate to avoid the loss of the diamond powder. With 10 to 14 mesh particles and sodium bicarbonate, and a fusion time of 30 minutes, a loss of 0.87% results. When the size of the particles is 200 to 325 mesh, and sodium bicarbonate is used with a fusion time of 30 minutes, the loss is 15% and that with 15 minutes as a fusion time is 7 to 8%.

Non refractory alumina [16, 10] can be readily brought into solution by sodium bisulfate fusion. This results in minimum loss of diamond powder. Fusion with potassium bisulfate and sodium fluoride removes fused aluminium oxide. The ratio of quantities of material to be cleaned is : potassium bisulfate: sodium fluoride :: 1 : 6: 1. The fusion is carried out in a silica crucible (no metallic vessel should be used) at a temperature of 400 °C with continuous stirring using a silica rod. The residue is dissolved in water and washed by decantation. The loss of diamond powder depends on the size. For example, when 100 to 250 mesh powder is present, the loss is 2%; for 250 to 400 mesh, the loss is 6%; and for 0 to 40 μm the loss is 11.4%.

G. Removal of Carbide Contaminants [15-16]: Fusion with potassium hydroxide or with sodium hydroxide is used to dissolve boron carbide. Potassium hydroxide is preferred because it results in small loss of diamonds. Details of the process are the same

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as mentioned under removal of metallic contaminants above (using fusion). To bring silicon [14] carbide into solution, fusion with sodium carbonate in a platinum crucible is carried out for 15 minutes. It is then leached with water and washed, followed by acid treatment to remove the decomposed silicon carbide. For this, it is heated cautiously with hydrochloric acid and a small quantity of sulfuric acid until decomposition is complete. The losses due to fusion are the same as mentioned in the case of ceramics.

Physical methods, such as removal of diamond powder from silicon carbide by skin flotation, may also be used. A mixture of diamond powder in potassium dichromate-sulfuric acid is warmed. Carefully, 95% of the solution is decanted and replaced with water. The beaker may be rotated to float the diamond powder on the surface of the liquid. If diamonds are still not free of silicon carbide, they are then fused with sodium carbonate as described earlier. Tungsten carbide may be removed by either acid treatment or fusion. For acid treatment, the powder is taken in a platinum dish to which nitric acid is added followed by 10% of its volume of hydrofluoric acid. The solution is heated and hydrofluoric acid is added until the reaction ceased. The diamond powder is then washed, decanted/centrifuged and dried.

For the fusion treatment, the powder to be treated is placed in a pyrex "Copper" flask and 10 to 15 times its weight of sodium bisulfate is added. The mixture is fused for 15 to 30 minutes and the melt is cooled and leached with hot strong sodium hydroxide solution to dissolve the precipitated tungsten oxide. It is then washed and dried. This is a convenient method and results in low loss. A 10 to 14 mesh diamond powder fused for 30 minutes results in 0.06% loss, while 15 minutes for fusion of 200 to 325 mesh powder results in 1.73% loss.

Common acids are not strong enough since tungsten carbide is chemically very inactive. One can use a mixture of nitric acid and hydrofluoric acid for dissolution of tungsten carbide. Also fusion with strong oxidizing agents such as sodium peroxide or a

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mixture of sodium hydroxide and potassium nitrate gives the required separation of diamond, but these methods are slow and expensive.

Recovery of diamonds from inserts [18] can be conveniently carried out by first oxidizing the inserts by heating them in a furnace until they break up into small fragments. These may then be dissolved in potassium or sodium hydroxide. The main disadvantage of the fusion process is that it requires the use of a considerable amount of alkali. The reaction between the molten hydroxide is very vigorous often resulting in evolution of a corrosive spray. Also, the leaching of the melt is a tedious procedure.

H. Removal of Glass [16]: Glass powder and fibres are brought into solution by fusion with potassium hydroxide in an iron pot. The sample is placed in a large iron pot with 10 to 15 times its weight of sodium or potassium hydroxide, and fused at a low heat for 15 to 30 minutes. Potassium hydroxide is preferred over sodium hydroxide owing to its lesser tendency to creep. It allows fusion to be completed in a shorter time. The molten mass is stirred continuously. After the fusion is completed, the mass is cooled and washed several times by decantation or by centrifuging and drying in an oven at 120 °C. If large quantities of glass are present, fusion may have to be repeated. To remove last traces of silica, a residue of diamond powder is dissolved in the mixture of hydrofluoric acid and sulfuric acid. Finally the powder is washed and dried.

I. Removal of Graphite [16]: To remove graphite, the sample is placed in a beaker with a small quantity of potassium chlorate dissolved in a minimum quantity of water. Nitric acid is added and the mixture boiled. If necessary, a few more additions may be made of this oxidizing mixture till all the graphite is destroyed. Then, the mixture is washed and dried.

J. Plastic contaminants [16]: Plastic impurities are decomposed by a mixture of potassium chlorate and sulfuric acid. The sample is placed in a large beaker and a small quantity of saturated solution of potassium chlorate is added. Nitric acid is added and the mixture is boiled thoroughly. Sulfuric acid is then added and the sample is evaporated

giving strong fumes to decompose all organic matter. For resistant materials, a few additions of nitric acid and potassium chlorate may have to be made, followed by the addition of sulfuric acid till the dissolution is complete. The loss of diamond due to the oxidizing mixture (i.e., when 10 to 14 mesh size diamond powder is present, and boiling time is 30 minutes), is approximately 0.45%. While in the case of 200 to 325 mesh size diamond powder, the loss is found to be approximately 5% for the same time of treatment.

Chemical methods were extensively used to treat polishing sludge. Although recovery is successfully achieved, the process is costly. This is not a desirable situation from the point of this project. Hence, these methods are not suitable and may only be used for preliminary investigation.

APPENDIX II

DETAILS OF ECONOMICS

Cost of a 11 centimeter diameter, 2.7 μm Whattman filter paper used is $ 0.10 (@ $ 10/100 numbers). Total electricity used for concentration of a 2 liter filtrate and for the stirring process (total time used for the concentration process is 1 hour and 45 minutes, using a 1000 W coil and 13 W for a 1/30 Hp motor used for the stirrer, and 250 W for the 1/3 Hp vacuum pump) is 1.75 X1000 + 1.75 X275 = 2231 Watt-hr. Cost of electricity, (@ industrial rate is $0.00054 /Watt hour), is $1.23 (the cost of electricity has been obtained from the City of Stillwater and has been assumed for a low voltage [240 volts] usage, since no need has been found to expect usage of increased voltage). These added together give $1.32 for 0.55 grams or 2.75 carats of diamond powder. The cost of this diamond powder @ $1.5/carat is $4.125. Hence, the cost to worth ratio is 0.32.

When the improved concentration process is used, the analysis is altered as follows. Filtration is found to be more economical when larger surface area is used. Based on the experience, these filter papers are used for filtering 30 to 40 liters of filtrate obtained from the primary filter. The membrane filter may be washed and reused at least 3 times.

Cost of a 0.2 μm, 11 centimeter diameter Whattman membrane filter (@ $90/25 membranes), is $4.25 each. But since the filter element is used for collection of fine particles, it can be reused. Thus, the cost is $4.25/30= $0.14 (for 2000 ml and considering that the membrane is used twice).

Cost of electricity is (for driving the 1/2 Hp pump and for driving the stirrer) ~$0.04. The cost of flocculant $10 per 100 grams. For the flocculation process, 0.3 grams is used

for 2000 ml of filtrate. Hence, cost of flocculant for 2000 ml is $0.03. Adding all the costs involved, the cost of 0.35 grams of diamond recovered (after removing the weight of flocculant) is $0.31, and its worth is $2.65 which gives a better cost to worth ratio of 0.12. Hence, it may be concluded that the latter method is better from economics and safety point of view since no boiler is used for the separation of diamond.

Costs involved in oil recovery are as follows. When 1000 ml of as-received sludge was treated, it resulted in ~800 grams of powdered sludge and 700 ml of reusable oil. Time taken is ~1 hour. A recent test used a 1/3 Hp high torque motor. Hence, adding costs of the 1000 W heater coil, pump and vacuum pump, the electricity cost is 1506 W-hr or $0.81 for 800 grams of powdered sludge. Since 100 grams of powdered sludge resulted in 19 grams of diamond powder, this may be distributed over 19 x 8=152 grams of diamond powder, resulting in ~ 0.07% of cost of the diamond powder. Thus, there is no significant change in the cost to worth ratio.

Grading of Diamond Powder [21, 22-23]

Grading the diamond powder may not be required since the diamond powder in the sludge is known to be 1 μm nominal. The following Table A I shows how these diamond powders are designated.

Based on the table, it can be concluded that it is reasonable to call it a sub-micron size diamond powder since, the larger particles undergo some cleaving and as a result, the number of such particles in the powder decreases.

TABLE A I

TYPICAL PARTICLE SIZE DESIGNATION OF DIAMOND POWDERS

Sl. No.	Range of particles, μm	Designation, μm
1	2 and less	1
2	1 to 5	3
3	4 to 8	6
4	6 to 10	8
5	8 to 20	14
6	20 to 40	30
7	30 to 60	45

APPENDIX III

FILTRATION PLOTS FROM TABLE V

Figures A1 to A5 show the effect of time on the filtration process. Each point represents ~100 ml of volume filtered. After studying these plots, the typical plots representing a specific set of conditions were identified and analyzed. The typical plots from different sets have been discussed in Chapter 4. Some of the factors affecting the filtration process and their effect on the process are discussed here. The effect of time, concentration of solution, and the relative number of fine and coarse particles are observed.

The plots given in Figure A1 are plotted before the T-P process. These show a characteristic progressive clogging and a low threshold time (~10 seconds) for the first 100 ml filtration (which remains almost constant at this value). The plots in Figure A2 are just after the first T-P process. These show the characteristic higher threshold (~25 seconds) and sections of the plot parallel to the X axis. Initially, the successive points parallel to the X axis are found more in number. These decrease in number with time while the time taken for filtration increases. Thus 'steps' are observed in these plots. Some successive points on a step may show variation in the time required for filtration, but the nature of the steps is consistent. If the suspension (decantant) is not sufficiently dilute, progressive clogging is observed to start after ~70% of the total number of points. It is evident from the Figure A 3 that dilution improves the filtration process. Threshold time decreases and due to presence of fine particles, steps are observed, though, in the later part of the test progressive clogging is observed indicating presence of larger particles. Figure A 4 shows filtration tests after the second T-P process. Characteristics are similar to the tests in Figure

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A 2 other than lower threshold. Figure A5 shows half area filtration tests. Inspite of dilution, the thresholds are higher indicating the concentration is relatively higher for the area of the filter paper in use.
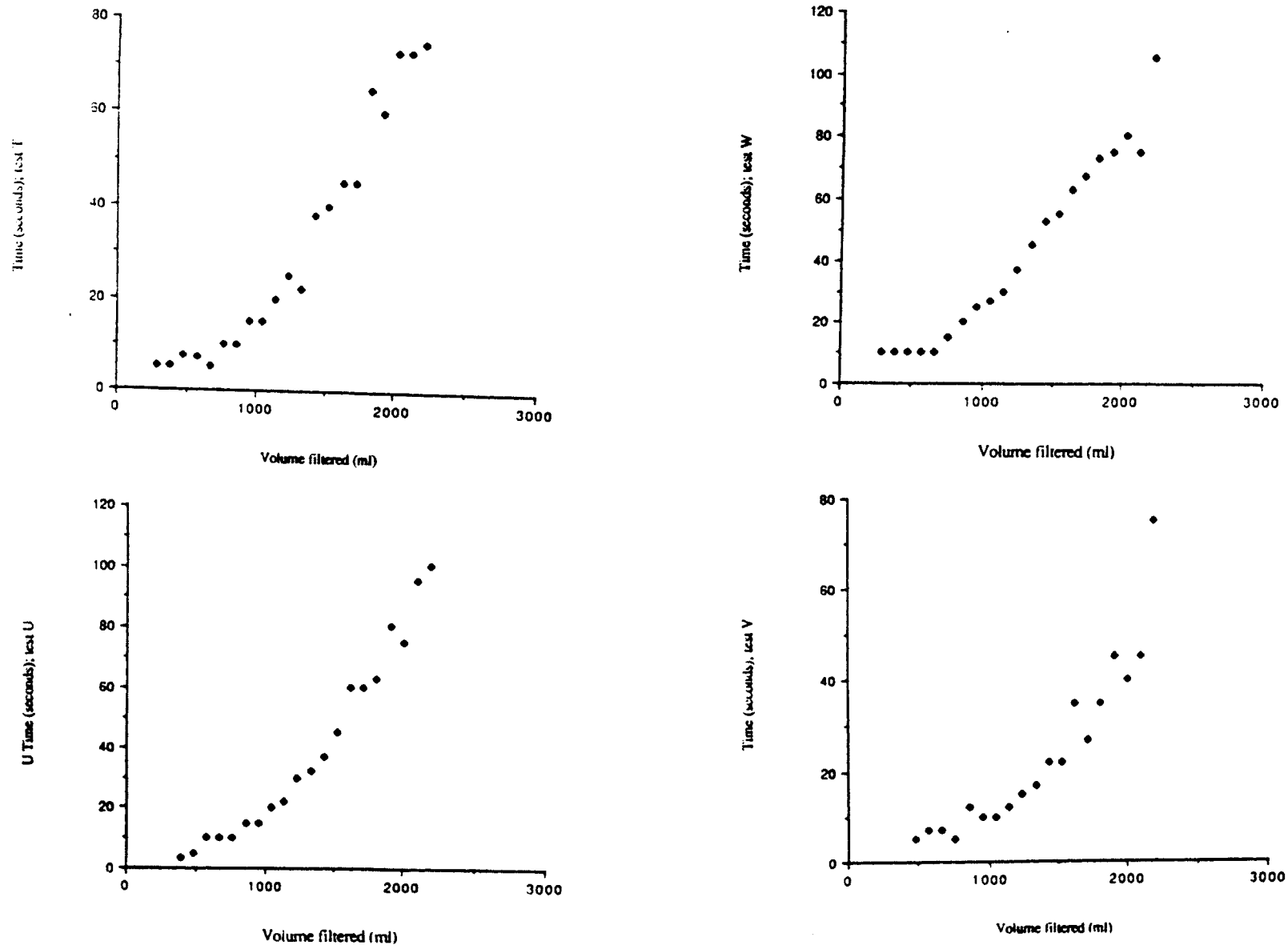
Figure A 1   Filtration Tests, Set II, Tests carried out Before the T-P process.
Plot shows progressive clogging of the filter paper after the initial 300 to 400
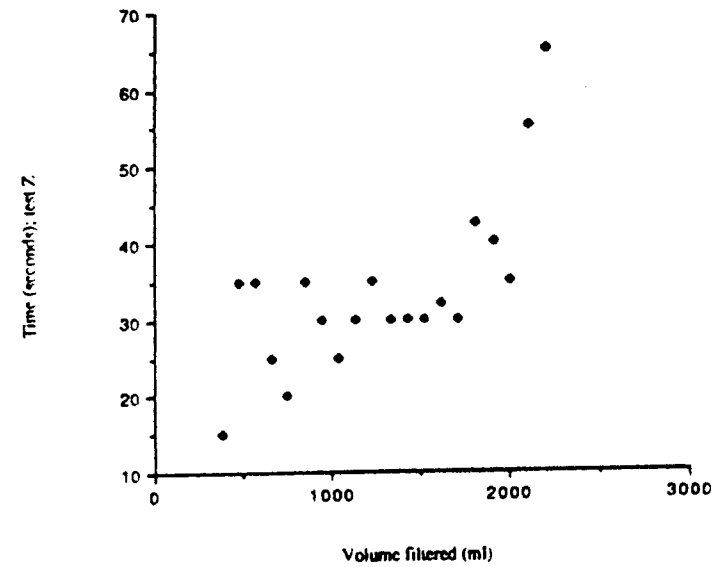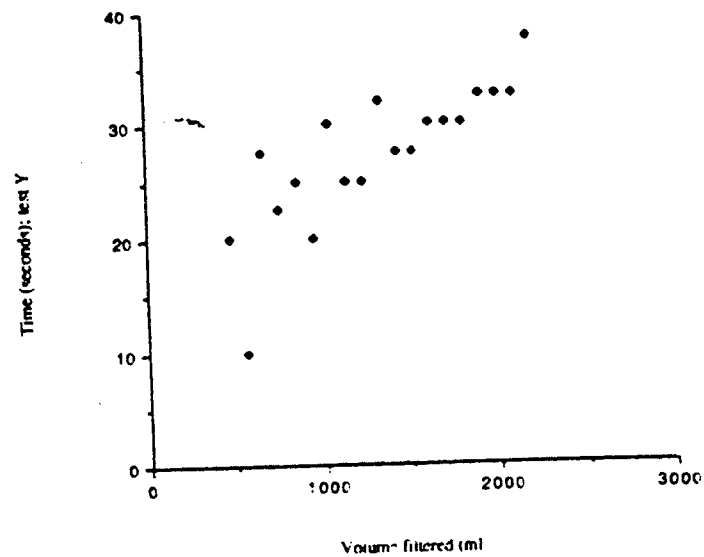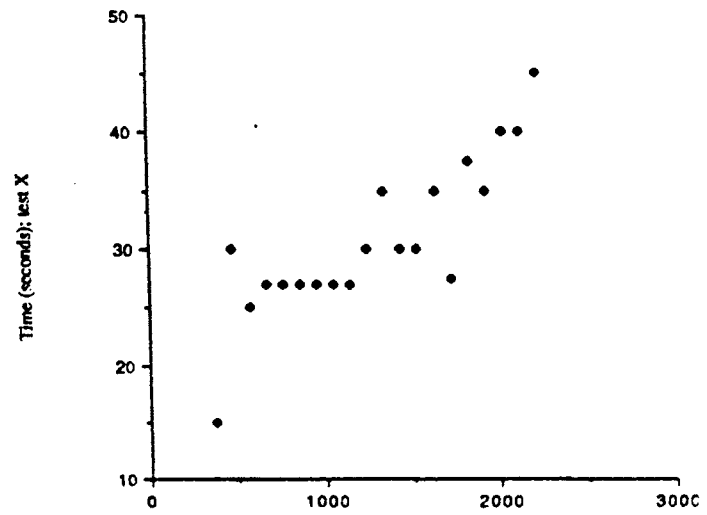ml of filtration. The typical progressive clogging is depicted in this plot.

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Figure A 2   Filtration Tests, Set II, Tests carried out After T-P process.
Plot shows same time for filtration for ~100 cc of the filtrate for 4 to 6 readings. Sections of the plot parallel to the X axis (steps) are typical of these plots.
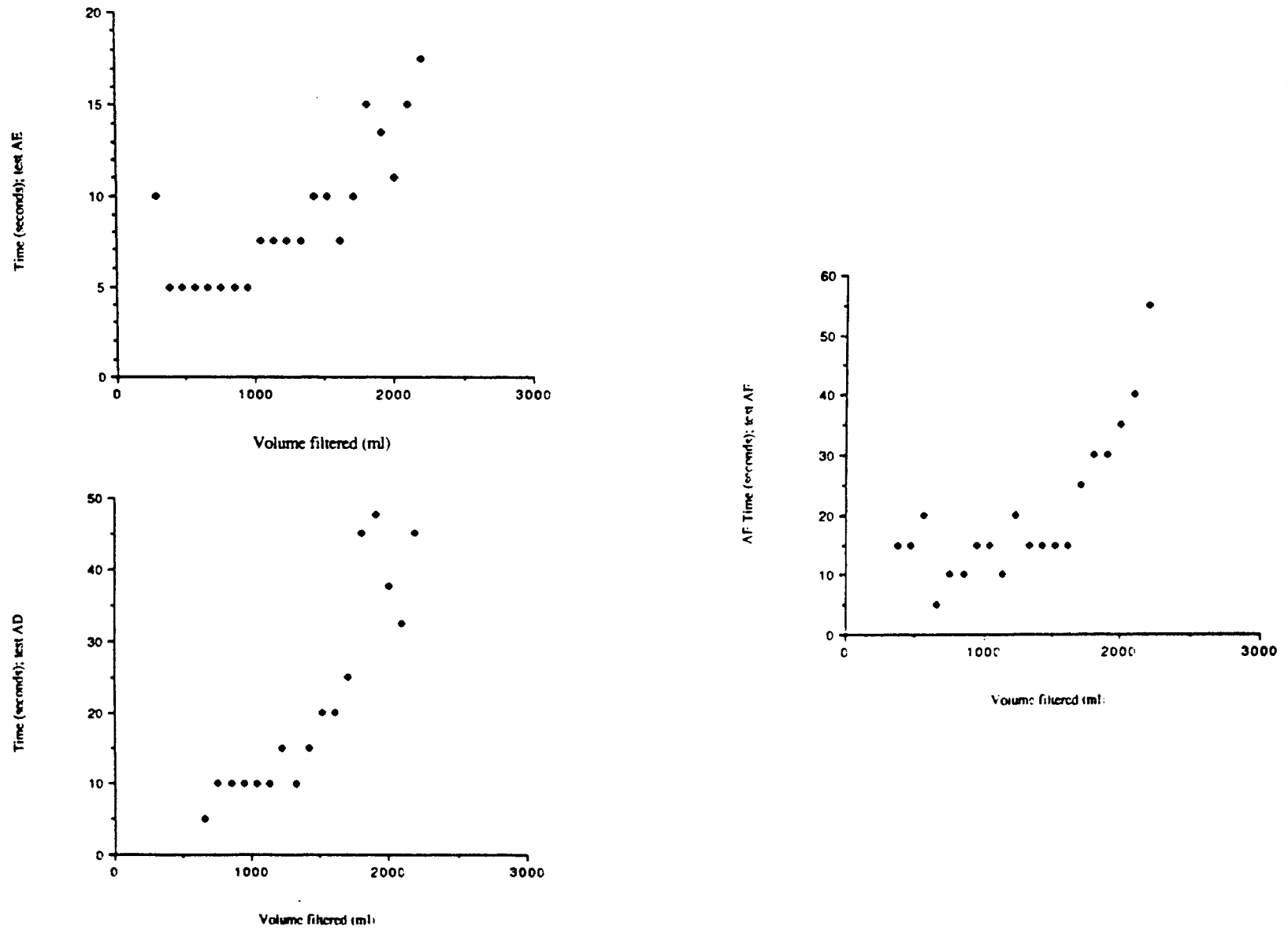
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Figure A 3 Filtration Tests, Set III, Tests carried out After T-P Process and After the
Experiments in Set II.
Plots show low threshold time (time required for first 100 cc to be filtered).
The presence of fine particles and dilute solution is indicated by the plot.
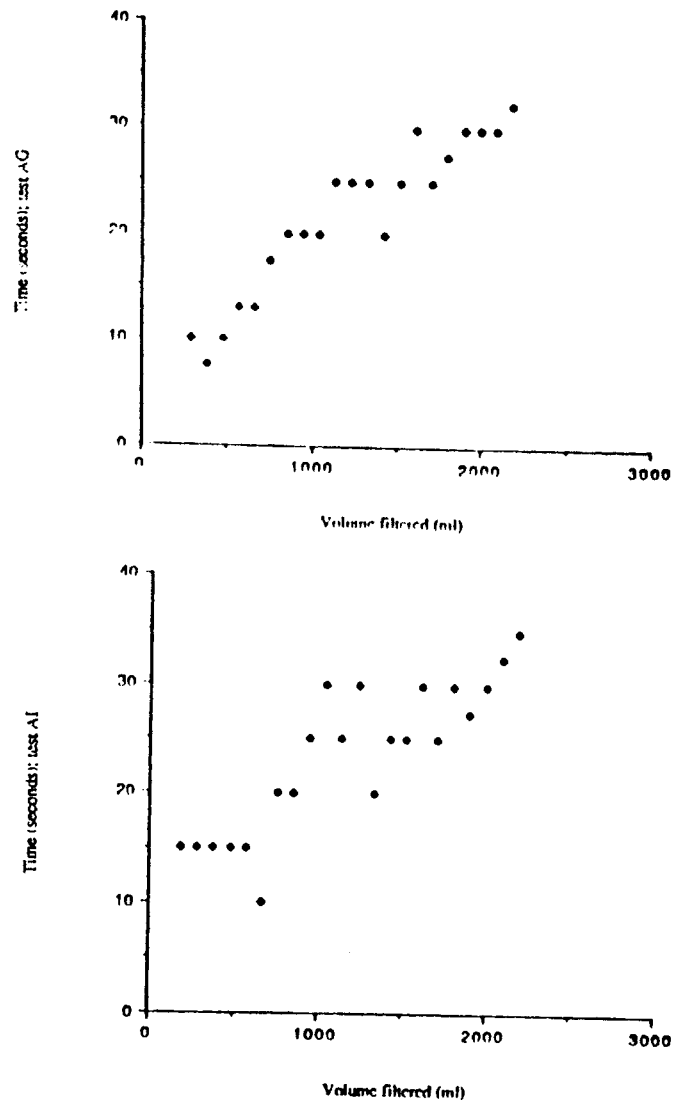
Figure A 4   Filtration Tests, Set IV, Tests carried out After 2nd T-P Process.
The number of fines have increased as compared to that in Figure A 3.
Solution is comparatively dilute relative to Set II. Threshold is 10 seconds
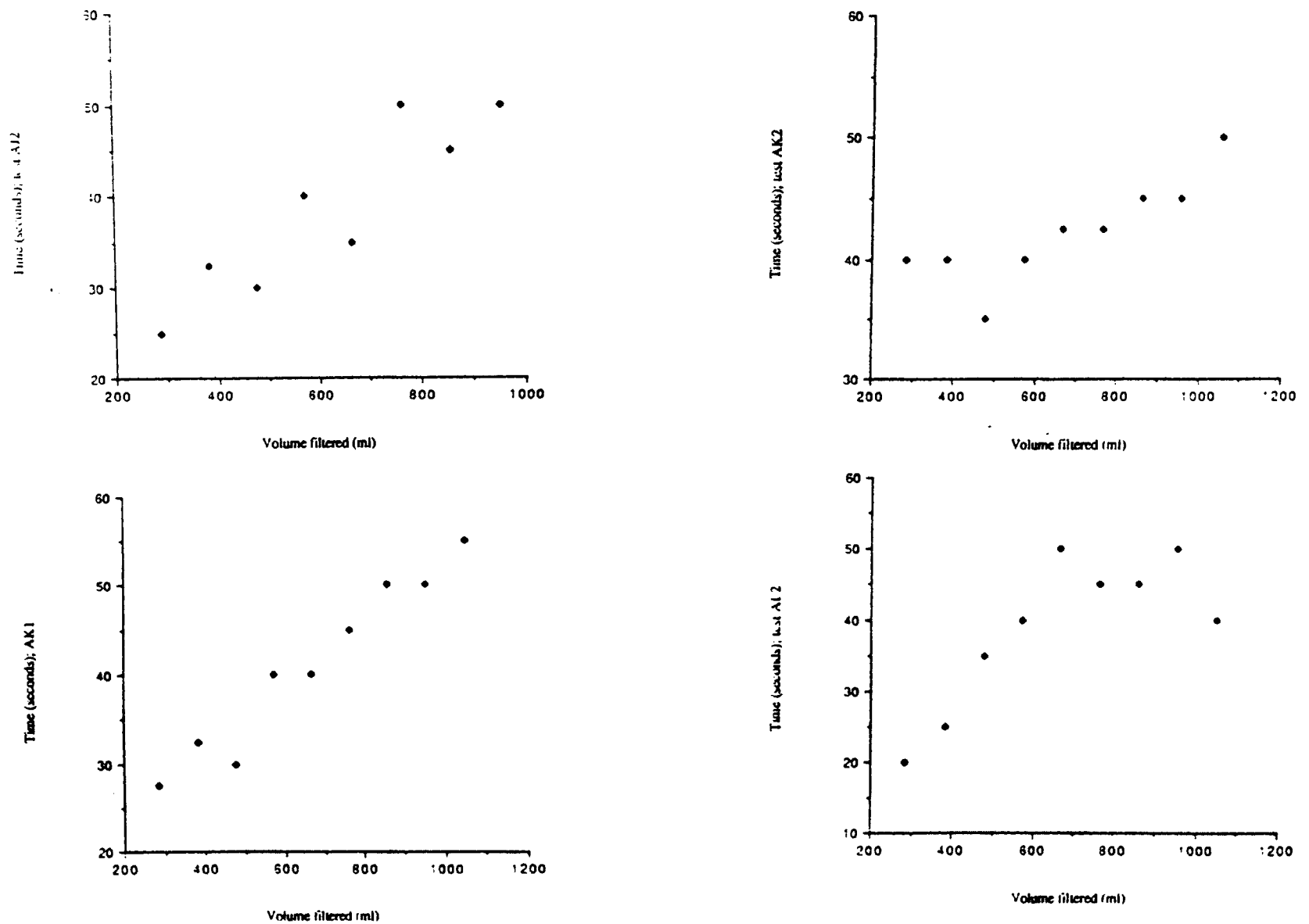indicating lesser fines as compared to Set II.

Figure A 5 Filtration Tests, Set V, Half Area Filtration Tests are Depicted.
The concentration of fine and coarse particles is high and threshold time is
found to increase to 30 seconds. Progressive clogging is also observed.

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VITA 2

Vivek Kumar Dubey

Candidate for the Degree of

Master of Science

Thesis: RECOVERY OF DIAMOND FROM POLISHING SLUDGE GENERATED IN FINISHING OF CEMENTED TUNGSTEN CARBIDE BALLS

Major Field: Mechanical Engineering

Biographical:

Personal Data: Born in Nagpur, India, July 3, 1966, son of Mahesh and Priti Dubey

Education: Graduated from Hislop College, Nagpur, India, July 1983; received Bachelor of Engineering Degree in Mechanical Engineering from Visvesvaraya Regional College of Engineering, Nagpur, India, in July 1988; completed requirements for the Master of Science at Oklahoma State University in May, 1994

Professional Experience: Research Assistant, Department of Mechanical and Aerospace Engineering, Oklahoma State University from January 1992 to January 1994. Engineer at Larsen and Toubro, India, responsible for the development of prototypes of components for high-pressure hydraulic systems for the earthmoving machines from August 1988 to July 1991.