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Separations Innovative Concepts: Project Summary

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SEPARATIONS INNOVATIVE CONCEPTS:
PROJECT SUMMARY

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Pacific Northwest Laboratory
Richland, Washington 99352

ABSTRACT

This project summary includes the results of 10 innovations that were funded under the U.S. Department's Innovative Concept Programs. The concepts address innovations that can substantially reduce the energy used in industrial separations. Each paper describes the proposed concept, and discusses the concept's potential energy savings, market applications, technical feasibility, prior work and state of the art, and future development needs.

SUMMARY

In 1982 the Office of Energy Systems Research within the U.S. Department of Energy (DOE) initiated the Innovative Concepts Program. The objective of this program is to identify immature concepts having the potential for saving substantial amounts of energy and to provide seed money for a preliminary investigation of their technical feasibility. This report provides information on the 10 innovative industrial concepts selected for further examination.

The approach used in this project assumes that a) good concepts come from experienced, knowledgeable investigators, b) innovators frequently generate more good ideas than can be used within their own organizations, and c) ideas are frequently generated in an organization unable to realize the benefits of further development. Therefore, other industrial organizations or federal agencies may be interested in providing financial support for further development of such concepts.

This project is an experiment in a continuing program to harvest creative, novel approaches to saving energy. This year's fair sought innovative concepts and inventions that could reduce energy consumption in industrial separations processes, specifically chemical processing, biotechnology separations, waste/fuel recovery, and process equipment. Approximately 2.7 quad of energy is consumed by U.S. industry in separations processes. That consumption is many times more energy than is required according to thermodynamic calculations.

Thirty-nine innovative proposals were received by the Innovative Concepts Program in response to the formal call for concepts. The ten that were selected to receive seed money and nonfinancial assistance are summarized below.

CHEMICAL PROCESSING

Liquid-Liquid Separation in Swirling Flows Using Friction-Reducing Polymers

The objective of this study was to explore the feasibility of separating small amounts of oil dispersed in water by using swirling flows. The approach depends on two physical effects that have not been exploited previously: 1) the occurrence of a central toroidal recirculation zone for large swirl numbers, and 2) the use of friction-reducing polymers to control the drop-size distribution.

The new separator design contains three distinct zones of separation. The resulting performance of the unique piggyback configuration is expected to give an equivalent two-stage effect. Therefore, compared with more conventional hydrocyclone designs for liquid-liquid separation, the proposed new concept has the potential for 1) higher efficiency per stage, 2) more flexible turndown characteristics, and 3) lower power requirements for an equivalent separation performance. Although the merits of the new separator have not been tested, a preliminary evaluation of the approach indicates that some of the above benefits are attainable.

Efficient Recovery of Finely Divided Mineral Particles by Centrifugation

An efficient process to recover heavy and finely divided mineral particles from light gangue minerals has been investigated by imposing a delicate balance between centrifugal and surface tension forces on these particles. A mixture of galena and silica fines of 400/500 mesh size was used in this study as a model system. Hydrophobic and heavy galena fines were separated easily from hydrophilic and light silica particles in water/organic liquid under centrifugal force. Better than 90% recovery with 85% purity was possible in a two-liquid system consisting of water and carbon tetrachloride with a centrifugal force less than ten times greater than the force produced by gravity.

BIOTECHNOLOGY SEPARATIONS

Biotechnology Separation of Pyrite from Coal

The use of microorganisms, particularly lithotrophic bacteria such as Thiobacillus (T.) ferrooxidans, was investigated as a cost-effective method for recovering coal that is currently discarded as being too dirty to burn. The bacteria are used to modify the surfaces of the pyrite particles contained in the sulfur. By altering the surface of the pyrite, it can be separated from the coal by the froth flotation process, a separation that would not be possible without pretreatment.

Experiments were conducted using two strains of lithotrophic bacteria, three species of nonlithotrophic bacteria, and one species of yeast. Results indicate that, while all microorganisms showed considerable ability to alter the pyrite surface and thus prevent flotation, the most effective was one of the strains of T. ferrooxidans, which produced nearly complete suppression. The tests also determined that the suppression is caused by direct cellular attachment and the action of intracellular enzymes, not by extracellular enzymes released into solution.

Periodic Cross-Flow Separation of Large Molecules, Especially Proteins, According to their Diffusion Coefficients

A method for separating relatively large molecules that have different diffusion coefficients has been developed. The molecules, in solution in their natural solvent environment, are separated by two mutually perpendicular coordinated flows, both periodic and bi-directional.

A mathematical model was developed and used to predict the performance of the method on a binary mixture of proteins in aqueous solution. The proteins are assumed to have molecular diffusion coefficients of 0.9×10^{-7} and 1.0×10^{-7} cm²/s. Separation is calculated to occur in 1 hour with recoveries and purities exceeding 99%. Calculations indicate that higher recoveries and purities may be readily achieved with somewhat more processing time; for example, 99.8% recovery and purity would require 2 hours of processing time. The feed protein concentration is approximately 0.4% w and the rate of processing is about 1 gram of protein per liter of separator channel volume per hour.

Recovery of Dilute Aqueous Butanol by Adsorption on Lignin

This concept addresses a novel technique for concentrating dilute aqueous butanol and acetone using lignin derived from sulfuric acid hydrolysis of biomass. Preliminary research has shown that lignin has the potential to selectively adsorb butanol, acetone, and perhaps ethanol from fermentation broth containing sugar and salts. After adsorption, the lignin can be regenerated by passing CO₂ gas at 90 C. The lignin was shown to retain its adsorption capacity after regeneration with CO₂.

WASTE/FUEL RECOVERY

Potential for Broader Applications of Extracting Hydrocarbons Using Liquid-Core Polyaphrons

A proposed concept is being developed to extract the bitumen from tar sands at low temperatures using liquid butane made up into a water-continuous polyaphron as the extractant. The preliminary evaluation of the proposed concept indicated that 1) tar sands represent a significant energy reserve; 2) hot water extraction as practiced in Alberta is energy intensive and unique in that many tar sands require different treatment; 3) aphrons made of kerosene or butane can effectively remove bitumen from tar sands that are not suited to hot water treatment; and 4) liquid butane in polyaphron form as the extracting solvent has potential for simple cold separation and can be recycled.

Fuel from Municipal Sludge

A proposed process is being assessed for separating a significant fraction of organic material from municipal sludge by acid extraction and for reconstituting the extracted organic material as a solid fuel. Experimental

results have demonstrated that 88% of the solids can be dissolved during acid extraction, and up to 25% of the initial solids can be precipitated when diluted with water. The precipitated product was a high organic (98% to 99%) solid and represented up to 38% of the initial organics.

Preliminary economic estimates show this process to be competitive with other sludge disposal and reuse alternatives for wastewater treatment plants serving one million people or more. The economic picture can be greatly improved by incorporating the negative cost of sludge disposal.

PROCESS EQUIPMENT

Development of an Electrostatic Agglomerator

The objective of this work was to analytically investigate an electrostatic agglomerator that is designed to control the fine particles in industrial processes and power plant flue gases. The results of the preliminary investigation of this concept indicate that the concept is feasible: particles can be charged and agglomerated, and the interparticle adhesion forces are strong enough to overcome collisional forces acting to break the agglomerates. The agglomerator can reduce both the energy consumption and the capital equipment costs of existing gas cleaning devices, and can reduce a respiratory health problem by increasing the efficiency of collecting submicron particles in existing filtration devices.

Large-Scale Generation of Microbubbles to Improve Flotation Processes and to Save Energy

A spinning cylinder currently is being tested as an alternative method for economically producing large quantities of high-quality colloidal gas aphanes. Preliminary results of bench-scale tests on the spinning cylinder indicate a considerable improvement in generating microbubble with good stability and bubble size, minimum void air, and reasonable operating cost. A larger unit has been designed and is being built for testing in this project.

Applications of a Magnetic Cyclone

This concept addresses two potential applications of a magnetic cyclone. The first application examines and demonstrates improved recovery of fine magnetite. The fine magnetite used in conventional dense media plants for coal cleaning is not fully recovered and recycled. The project results show that the magnetic cyclone can recover dense media magnetite (as purchased by operators of dense media coal cleaning plants) effectively without excessive magnetic fields or feed pressures. However, when samples from process streams of coal cleaning plants were used, the recoveries were lower than with pure magnetite, largely because of the very fine size of the magnetic particles in the process streams. Additional tests will examine cyclone geometry and magnetic field variations to further improve the magnetic cyclone recovery of these fine particles.

The second application concerns the dewatering of steel plant sludges to allow these iron-bearing materials to be disposed of or reused. To date a literature search has been undertaken to determine the characteristics and potential of this application. However, because appropriate plant samples were not available in time to complete test work. That work should be completed by the end of April 1988, when a complete report will be made available.

ACKNOWLEDGMENTS

The Separations Innovative Concepts Fair is the result of the efforts of several individuals and organizations. Funding for this project was provided by the U.S. Department of Energy's (DOE's) Office of Energy Utilization Research under the direction of John J. Brogan. Terry Levinson in the Energy Conversion Utilization Program was the Program Manager at DOE. We gratefully acknowledge the cooperation of DOE's Office of Industrial Programs.

Some of the recent improvements in the Innovative Concepts Program are due to the opportunities presented by the close administrative relationship with the Energy-Related Inventions Program, led by A. Jack Vitullo at the DOE and by George Lewett at the National Bureau of Standards.

Several staff members at PNL were involved in structuring the overall research effort, for writing and evaluating the procurement documents, screening the proposals, making arrangements for the Fair, and preparing materials for the Fair: Mark Anderson, Carol Bruneau, Robin Eckert, Bobi Garrett, Joe Hauth (patent attorney), Ron Smith, Steve Smith, and Sue Vickerman.

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INTRODUCTION

The initiation of invention/innovation needs to be accelerated in the United States in order to speed up the entire process of technology transfer. During the past several years, business leaders, engineers, scientists, and lately, politicians have recognized that our industrial competitiveness has been deteriorating while our excellence in research continues. This trend has produced a growing consensus that we must improve our ability to bridge the gap between research and the marketplace in the United States. We can no longer afford the patterns of the past where innovative technology trickled out into the marketplace in a serial process that took as much as 25 years. International competitors are bringing technology into the marketplace in months instead of years. Many solutions are being proposed to accelerate technology into the marketplace. Acceleration of the latter stages of this process is already occurring.

The Department of Energy (DOE) established the Innovative Concepts Program (ICP) in the Office of Energy Utilization Research (EUR) in 1983 after two years of planning. The ICP objective is to develop and demonstrate methods for identifying and encouraging the growth of immature concepts having the potential to save energy and increase productivity through innovative approaches fundamentally different from current practice. The ICP is encouraging the first steps of the invention/innovation (technology transfer) process.

Pacific Northwest Laboratory (PWL)^(a) operates this program for the DOE to identify long-range, high-payoff concepts to:

- provide a bridge between fundamental scientific progress and the technology areas of EUR
- identify large energy-saving improvements to eliminate energy-intensive activities.

The program is designed to accomplish these tasks by the following activities:

- identifying a focus area (for example, industrial processes) for a cycle of innovation
- soliciting concepts in this focus area and selecting a limited number for further investigation
- providing modest funding to innovators for investigating the concepts' technical and business potential
- personally visiting each inventor to provide encouragement and concrete suggestions for making the most efficient use of the limited funding
- introducing the selected concepts to potential sponsors.

This document is provided to assist potential sponsors in their search for worthwhile industrially oriented products or programs.

Innovators who originated these concepts received approximately \$15K to perform a preliminary investigation of the technical and business potential of a concept. A preliminary investigation sometimes proves that a concept is not technically feasible. On the other hand, it may reveal sufficient information to show that the concept should be developed further.

The original goal was to have 10% of the concepts accepted for funding by ICP to receive follow-on funding by other programs or organizations. This is the third funding cycle sponsored by the ICP. Twelve buildings concepts and 10 industrial process concepts were funded and presented in two technology fairs, Buildings Innovative Concepts in May of 1984 and Industrial Innovative Concepts in November of 1985. Six of those 22 concepts received

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substantial follow-on funding from other sources. Two of the six resulted in the formation of spin-off companies. Several additional concepts are being actively considered for follow-on funding.

In this funding cycle, ICP sought innovative concepts and inventions that could reduce energy consumption in industrial processes: chemical processing, biotechnology separations, waste/fuel recovery, and process equipment.

CHEMICAL PROCESSING

1.0 LIQUID-LIQUID SEPARATION IN SWIRLING FLOWS USING FRICTION-REDUCING POLYMERS

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ABSTRACT

The objective of this study was to explore the feasibility of separating small amounts of oil dispersed in water by using swirling flows. The approach depends on two physical effects that have not been exploited previously: 1) the occurrence of a central toroidal recirculation zone for large swirl numbers, and 2) the use of friction-reducing polymers to control the drop-size distribution.

By introducing a dilute dispersion into a vortex field as an annular swirling jet, a toroidal recirculation zone forms about the axis of the vortex. This secondary flow provides a novel means to capture oil droplets from the main flow field and to redirect them to an effluent orifice. Turbulent fluctuations on the axis of the vortex and within the central toroidal recirculation zone may cause the liquid drops to break into finer drops. However, by injecting a high molecular weight polymer into the core region of the vortex, turbulent fluctuations are dampened. If this stabilizes the internal drop-size distribution, then a more efficient separation will result.

The new separator design contains three distinct zones of separation. The resulting performance of the unique piggyback configuration is expected to give an equivalent two-stage effect. Therefore, compared with more conventional hydrocyclone designs for liquid-liquid separation, the proposed new concept has the potential for 1) higher efficiency per stage, 2) more flexible turndown characteristics, and 3) lower power requirements for an equivalent separation performance. Although the merits of the new separator have not been tested, a preliminary evaluation of the approach indicates that some of the above benefits are attainable.

The potential impact of the new proposal for de-oiling water on offshore platforms is significant because only two manufacturers currently offer a product for this application. A six-month study is needed to evaluate the technical performance of the new separation concept and to develop a prototype device for field study. The relative merits of the new approach will be compared with the performance of other hydrocyclone technologies currently being used.

1.1. INTRODUCTION

Hydrocarbon contamination of the oceans and estuaries is obviously undesirable, and emission standards for discharging bilge water from oil tankers and formation water from offshore platforms are challenging the available technology (Johnston and Halliwell 1976; Lucas 1975).

Currently, 38 ppm by volume is the allowable daily average concentration of free oil in the discharge water from platforms in the Bass Strait near Melbourne (Hayes, Carroll and Fothergill 1985). In the Gulf of Mexico, 48 ppm is the allowable monthly average oil and grease concentration in produced water (Final NPDES General Permit 1986). As the amount of water increases with the production of crude oil, these necessary environmental standards may, unfortunately, limit the economies of this industry. Therefore, a clear need exists for an efficient oily water cleanup system for offshore production of oil (Hayes 1985; Koons, McAuliffe and Weiss 1976).

For the past 20 years, Thew and his coworkers at Southampton University (UK) have been developing improvements to the hydrocyclone for de-oiling water (Colman and Thew 1980, 1983, 1984; Colman, Thew and Corney 1980; Nezhati and Thew 1987). The hydrocyclone is well established in the chemical, food, and mineral industries as an

inertial separator or classifier of solid particles (Bradley 1985; Svarovsky 1984). Now, because of Thew's efforts, it is also becoming an acceptable alternative to other unit operations as a liquid-liquid separator.

Because immiscible fluids generally have low relative densities, very intense swirling flows are needed to separate a finely dispersed liquid phase by centrifugal action. Centrifugal acceleration is produced within a hydrocyclone by introducing the feed stream tangentially into a conical device under high pressure (see Figure 1.1). The kinetic energy of the feed is large and the flow is turbulent. Fluid shear may break up large drops into smaller drops and, in some cases, may even cause a "stable" emulsion to form (Bradley 1985; Robertson et al. 1984). This phenomenon, probably more than any other factor, has limited the widespread use of hydrocyclone technology for liquid-liquid separation.

In a hydrocyclone used to separate small amounts of oil from water, the dispersed oil phase migrates toward the axis of the swirling flow field and is removed with the overflow stream. In the Southampton design, the

FIGURE 1.1. Conventional Hydrocyclone Geometry for De-oiling Water

overflow ratio Q_o/Q_F may be as small as 0.01. Back pressure on the overflow and underflow effluent streams is necessary to prevent air entrainment into the oil phase. In this situation, unlike many other applications of hydrocyclones, an air core does not appear on the axis of the vortex. Instead, large jet-like countercurrent axial flows develop between the vortex finder and the apex region, depending on the magnitude of Q_o/Q_F (see Dabir 1983; Chen 1987).

The potential of hydrocyclones for separating a light dispersed phase from a heavy continuous phase is explained by equating the residence time of a droplet in the swirling flow to the time needed for the droplet to migrate to the axis (Van Rossum 1953; Listewnik 1984). For purposes of illustration, suppose the flow within the hydrocyclone chamber is a "free" vortex with a uniform axial velocity. The tangential and axial components of the mean velocity are

$$\langle u_\theta \rangle = u_F R_c / r \quad (1)$$

$$\langle u_z \rangle = Q_u / A_u \quad (2)$$

where u_F = bulk average velocity of the feed (Q_F/A_F)

A_F = cross sectional area of the tangential inlet tube

A_u = cross sectional area of the axial underflow effluent tube

R_c = radius of the hydrocyclone chamber at the feed entry

r = radial distance from the axis of the vortex field.

If the local centrifugal force acting on a liquid drop is balanced by viscous drag, then the drift velocity of the dispersed phase is

$$u_D = \frac{\ell^2 (\rho_D - \rho_c) \langle u_\theta \rangle^2}{18\mu_c r} \quad (3)$$

where ℓ = diameter of the liquid drop

μ_c = viscosity of the continuous phase

ρ_D = density of the dispersed phase

ρ_c = density of the continuous phase

r = radial distance from the axis of the vortex field.

Because $\rho_D < \rho_c$ for a "light" oil in water, u_D is negative and the dispersed phase migrates toward the axis of the swirling flow.

An explicit relationship between the particle size which has enough time to migrate to the axis of a vortex of length L follows by combining Equations (1) through (3). If $A_u = A_F$ and $Q_u = Q_F$ (de-oiling water), the resulting analysis yields

$$\left(\frac{\ell^*}{R_c} \right)^2 \left(1 - \frac{\rho_D}{\rho_c} \right) \left(\frac{Q_F u_F}{\mu_c} \right) = 4.5 \quad (4)$$

where L = length of the vortex

ℓ^* = diameter of a particle which starts at $(r, z) = (R_c, 0)$ and migrates to $(r, z) = (0, L)$.

Figure 1.2 shows the behavior of Equation (4) for parameters that are characteristic of de-oiling water in the Southampton hydrocyclone (i.e., $R_c = 35$ mm, $L/R_c = 48$). For $u_F = 3.5$ m/s and $D_c/D_F = 4$, the Reynolds number for the flow in the tangential inlet tube is 61,250. Obviously, the flow is highly turbulent for volumetric flow rates of industrial interest ($Q_F = 50$ L/min).

Because particles smaller than d^* do not have enough time to reach the axis, the probability that they will be removed with the reverse flow stream decreases significantly. Equation (4), reported here for the first time, is consistent with the observed performance of the Southampton hydrocyclone under laboratory as well as field conditions (Thew 1984, 1987). Thus, for a fixed value of u_F , the equation helps to explain why de-oiling hydrocyclones must be longer than conventional hydrocyclones in order to capture particles as small as 50 microns. However, Equation (4) stems from an oversimplified view of the flow and does not include important hydrodynamic phenomena associated with the viscous nature of the vortex core or the effect of turbulence on droplet breakup and dispersion.

The conclusion from Equation (4) that the separation efficiency can be increased for a fixed value of u_F by simply increasing L/R_c may be misleading. Experimental and theoretical studies of vortex flows operating without air cores indicate that near the axis an outward radial flow occurs (Dabir 1983; Chen 1987). Therefore, because of viscous drag, very fine oil droplets may be unable to penetrate the core of the flow field even for very long residence times. This phenomenon, illustrated by Figure 1.3, partly motivates the proposal that the dispersed phase should be introduced closer to the axis of the vortex (see Section 1.2).

FIGURE 1.2. Critical Separation Size Based on Particle Residence Time Within A Free Vortex

For $r \gg 0$,

$$\langle u_\theta \rangle = Kr^N$$

$$N = -0.75$$

$$K = 500 \nu_e \text{ cm}^{1-N}/\text{s}$$

$$\nu_e = 10 \nu, \text{ 'eddy' viscosity}$$

$$\nu = 0.01 \text{ cm}^2/\text{s}$$

$$\rho_D/\rho_C = 0.9$$

NOTE: These calculations illustrate the classification action of a viscous vortex. At $z = 10$ cm, a $6 \mu\text{m}$ particle is located at $r = 0.2$ cm, whereas a $32 \mu\text{m}$ particle is on the axis ($r = 0$). For $z > 25$ cm, the particles are no longer separated. [Based on a similarity solution to the Navier-Stokes equation for jet-like flow (p. 160, Chen 1987)].

FIGURE 1.3. Droplet Equilibrium Orbits Within a Viscous Vortex

Although the hydrocyclone is a relatively simple and inexpensive unit operation, its performance as a liquid-liquid separator is directly affected by four syndromes:

1. large-scale secondary flows that remix the separated dispersion
2. turbulent fluctuations that cause remixing and drop breakup
3. an inverse relationship between the separation force and the time available for separation
4. particle equilibrium orbits within the core of the vortex.

Many variations in the basic design of hydrocyclones have been introduced to compensate for one or more of these factors (Bednarski and Listewnik 1987; Thew 1987). Thew eliminated the large-scale secondary flows in the upper part of the hydrocyclone by using a larger than 'normal' swirl chamber and a tangential feed with a lower kinetic energy (see Figure 1.1). This also lowers the turbulent intensity at entry.

To compensate for the lower centrifugal force, the conical section of the Southampton design, which amplifies the swirl component of the flow, is much longer than conventional hydrocyclones used for other separation problems. However, the flow remains turbulent and large oil droplets can still be torn apart by turbulent fluctuations. Therefore, because of the phenomenon illustrated by Figure 1.3 and because turbulence always produces a fine dispersion of drop sizes, the modified design of Thew has unavoidable intrinsic limitations. A different approach is needed to simultaneously resolve the above syndromes of hydrocyclone technology for liquid-liquid separations.

1.2 ASSESSMENT OF THE CONCEPT

A small amount of polyethylene oxide in water (<100 wppm) has a significant effect on the properties of turbulent flows (Virk 1975; Sellin and Moses 1984). For small capillary tubes, an order of magnitude reduction in the friction factor can occur; for larger pipes of industrial interest, the effect is smaller but still significant. Generally, any linear, flexible, macromolecule having a molecular weight larger than 500,000 is an effective drag reducer in dilute solutions. Although the specific physical mechanism underlying this phenomenon remains unclear, the practical consequences are clear: turbulence is moderated. Thus, trace amounts of polymer injected into the core region of a flooded (no air core) hydrocyclone may dampen turbulent fluctuations that cause liquid drops to break into smaller drops. Moreover, the polymer may also stabilize the central core flow and, thereby, permit even smaller overflow ratios (i.e., Q_o/Q_F in Figure 1.1) than the Southampton design.

Liquid-liquid separations in swirling flows may also be improved significantly by exploiting more directly certain flow patterns that develop within the core region of a vortex. For example, when the characteristic swirl number, defined by

$$S = \frac{(\text{AXIAL FLUX OF SWIRL MOMENTUM})}{(\text{AXIAL FLUX OF AXIAL MOMENTUM})(\text{TRANSVERSE LENGTH SCALE})}$$

is large, the radial and axial pressure gradients cause a central toroidal recirculation zone to form (Gupta, Lilley and Syred 1984). Figure 1.4 shows the effect of S on a swirling jet and on a swirling annular jet. The phenomenon shown is widely exploited to stabilize combustion flames, but is generally avoided in conventional cyclone separators.

Another pervasive feature of swirling flows is their large resistance to contractions compared with their non-swirling counterparts. A vortex valve exploits this fact by injecting a small secondary (or control) flow tangentially into a conduit and allowing the flow to contract radially (Lewellen 1971). The swirling action of the fluid is amplified because of a tendency to preserve angular momentum. Thus, a large back pressure develops within the valve and the flow rate decreases significantly. A hydrocyclone, which obviously has a different

FIGURE 1.4. Central Toroidal Recirculation Zone (CTRZ) at High Swirl Numbers (Gupta, Lilley and Syred 1984)

function than a flow valve, can be viewed as a vortex valve with the entire feed stream being used as the "control" flow component. Is this the most energy efficient way to operate a hydrocyclone for liquid-liquid separations?

In the following sections, the proposed concept is described, and its technical feasibility, benefits, and status are discussed.

1.2.1 Description of the Concept

The purpose of this study is to introduce and to partially evaluate the potential of a new separation concept for de-oiling water that exploits directly some unique flow structures within vortex flows. The goal is to develop a hydrocyclone separator capable of removing small amounts of oil ($<3,000$ wppm) dispersed as fine droplets in water.

Figure 1.5 illustrates a new approach to liquid-liquid separation when the dispersed phase is lighter than the continuous phase (oil in water). The proposed method attempts to exploit two unrelated physical effects: 1) some novel secondary flows at high swirl numbers, and 2) the ability of high molecular weight polymers to reduce turbulent fluctuations.

For a light dispersed phase, a liquid droplet in the vortex field tends to move toward the axis until it encounters its equilibrium orbit (see Figure 1.3). The conventional approach is to introduce the entire feed tangentially into the outer region of the flow in order to drive the vortex. Thus, the major operating cost of this unit operation is associated with the large pressure drop (centrifugal head) needed to inject the feed into the "free" vortex region of the flow field. This strategy may be unnecessary for good separation of a light dispersed phase. The new approach suggested by Figure 1.5 is to introduce the feed closer to the axis of the vortex as a swirling annular jet while using a particle-free control flow to supply supplemental energy to the vortex. Like the vortex valve and the conventional hydrocyclone, the swirling action of the confined flow is amplified by using a conical geometry.

For large swirl numbers, separation of the light dispersed phase from the continuous phase occurs in three zones: A) within the annular feed tube, B) within the central toroidal recirculation zone at the entry of the overflow effluent tube, and C) within the contraction zone of the flow field near the underflow effluent tube. To control the turbulent fluctuations within the vortex core, small amounts of a high molecular weight polymer (such as polyethylene oxide) can be injected into the reverse jet-like flow running from the apex toward the central toroidal recirculation zone. By reducing the intensity of turbulence within Zone C (see Figure 1.5), we anticipate that larger drops can form by coalescence, that the vortex core may be less susceptible to breakdown, and that the rate of energy dissipation within the core region will be lower.

The above concept, which represents a combination of several ideas, will have its own unique set of limiting syndromes, yet to be identified. However, the proposed device attempts to address two specific problems associated with separating a fine suspension of a light liquid phase from a continuous liquid phase with a small difference in density (i.e., oil in water):

- the need for a large centrifugal acceleration
- the need to control drop breakup by turbulent fluctuations.

The first problem is approached by introducing the dispersed phase nearer the point of ultimate separation (see Figure 1.5), whereas the second problem is approached by using friction-reducing polymers.

1.2.2 Technical Feasibility

The technical feasibility of the new centrifugal separator is discussed below in terms of its piggyback configuration, central toroidal recirculation zone, polymer injection, and power requirements. Also, impediments to widescale use and potential markets for the concept are discussed.

FIGURE 1.5. Schematic of the New Separation Concept

Piggyback Configuration

One of the simplest measures of separation performance is the fraction of oil removed from the feed:

$$\epsilon_u = \frac{Q_F c_F - Q_U c_U}{Q_F c_F} = 1 - \frac{c_U}{c_F} \quad (5)$$

The de-oiling hydrocyclone developed at Southampton University (see Figure 1.1) gives $\epsilon_u = 0.85$ for conditions of commercial interest (Thew 1984, 1986, 1987). In the absence of droplet breakup phenomena, the overall separation efficiency can be increased to 98% by using a second stage. This may not be practical if the underflow stream from the first stage must be repressurized.

Although the separation concept defined by Figure 1.5 has not been evaluated yet, we expect $\epsilon_u = 0.97$ for a single pass under the same conditions for which the more conventional design gives $\epsilon_u = 0.85$. The reason for this is that the piggyback configuration of the new design has three distinct zones of separation: primary (Zone A), secondary (Zone B), and tertiary (Zone C). Because the "light" phase always drifts toward the axis, this strategy for introducing the feed into the vortex chamber should give an equivalent two-stage effect. The primary separation of the oil droplets within the annular feed tube could be enhanced further by using a hydrophobic material for the vortex finder (Sheng, Welker and Sliepcevich 1974). We are hopeful that the geometric scales of the proposed design can be selected to reduce the concentration of oil from 1,000 wppm to 30 wppm with only a single pass through the separator (see Section 1.3.1).

Central Toroidal Recirculation Zone

Separation Zone B occurs for large swirl numbers (see Figure 1.2). The suggestion that this secondary flow can capture oil droplets and direct them toward the vortex finder orifice is intriguing, but speculative. The strength of this strategy must be evaluated carefully because the potential for drop breakup within the central toroidal recirculation zone seems likely. On the other hand, this secondary flow may provide a positive stabilizing influence on the vortex core and, thereby, permit a lower effluent ratio Q_o/Q_F .

Polymer Injection

The Gulf of Mexico oil fields produce nearly 800,000 bbl/day of water and about the same amount of oil (Burke 1985). Therefore, because of the large amounts of water produced on offshore platforms, it is important to determine the most effective way to use friction-reducing polymers for turbulence control. The strategy proposed here attempts to dose only the reverse flow portion of the flow field ($\approx 0.1 Q_F$) where the turbulence dissipation rate is highest. If the polymer cost \$3 per lb, then the cost for chemicals needed to dose 80,000 bbl/day of water at 100 wppm is \$8,400 per day. Thus, the cost per barrel of oil produced is about 1.05 cents. Obviously, if friction-reducing polymers can prevent drop breakup, then the polymer should be introduced into the flow field where it has the largest impact.

Power Requirements

Because the centrifugal head determines the pressure drop across a hydrocyclone (Bradley 1965), the power required by the new separator may be less than the power required by the more conventional approach (Figure 1.1). The conjecture here is that the piggyback configuration needs a smaller centrifugal acceleration to achieve the same degree of separation. However, this feature has not yet been demonstrated.

Impediments to Widespread Use

Because of the high shear fields within hydrocyclones, breakup of drops can occur. This phenomenon has prevented the widespread adoption of the hydrocyclone for liquid-liquid separation. Careful design of the entry region and the initial swirl chamber (see Figure 1.1) provides some improvements. However, at very high flow rates, intrinsic turbulent fluctuations can still decrease the mean particle diameter and form a "stable" emulsion. The use of a polymer additive to prevent drop breakup complicates the unit operation. Continuous injection of a concentrated polymer solution into the core and subsequent mixing with the fluid in Zone C (see Figure 1.5) may upset the flow patterns and the anticipated separation effect.

Friction-reducing polymers are expensive (\$1 to \$3 per lb). If the process feed rate is large, then adding enough polymer to the entire feed to make a 100 wppm solution would be too costly and wasteful. Local injection

of polymer into Zone C, although awkward, reduces the quantity of chemicals needed by an order of magnitude. Polyethylene oxide and polyacrylamide are already used as flocculating agents in waste water treatment facilities. At low concentrations, these chemicals have a negligible impact on the environment (Dow 1975; Union Carbide 1985). Thus, by using a local injection strategy in which only 10% of the feed rate is treated with polymer, the back-mixed concentration of polymer in the clean water will be much less than 100 wppm.

Potential Markets

The separation concept described in Section 1.2.1, if feasible, would have an immediate impact on cleaning oily water on offshore platforms. Three companies manufacture hydrocyclone type equipment for this application: BWN (Australia), Serck Baker (UK), and Alstom (France). Recently, BWN purchased the Oilspin^(a) technology of Serck Baker (1984). The Vortoil^(b) (BWN 1987) and Oilspin designs stem directly from the Southampton work. Alstom (1987) uses a rotary de-oiling cyclone (Dynaclean)^(c) which is a hybrid between a centrifuge and a cyclone. The reported separation efficiency of the rotary separator is higher than the more conventional hydrocyclone design (Figure 1.1) presumably because spin-up of the fluid mass is gentle (Gay et al. 1987).

If the piggyback design (see Figure 1.5) together with the central toroidal recirculation zone causes the separation of very fine oil droplets ($<30 \mu\text{m}$), then this new compact separator could also be used to clean bilge and ballast water on ocean vessels as well as other waste streams presently being cleaned by more costly unit operations.

1.2.3 Benefits of the New Concept

As a compact separator, the hydrocyclone offers many new opportunities for liquid-liquid separations (Goldberger 1973). Depending on the specific application, it would either compete with, or complement, other technologies such as gravity separators, filters, parallel plate coalescers, gas flotation, and centrifuges (Wyer, Van Cleave and Biglane 1975). Possible, yet unproven, benefits of the specific concept shown by Figure 1.5 relative to the hydrocyclone shown in Figure 1.1 are as follows:

- stable drop-size distribution - This may result by using polymers to decrease the turbulent intensity and by introducing the dispersion into the vortex chamber at a lower pressure.
- lower overflow ratio - This may result by introducing the feed as an annular jet and causing a central toroidal recirculation zone to form near the overflow orifice.
- higher efficiency per stage - This may occur because the piggyback configuration provides three zones for separation.
- flexible turndown characteristics - The use of a control flow component to supplement the energy needed for the vortex action partly uncouples the feed rate from the separating force.
- lower power requirements for equivalent separation performance - This may occur because the dispersion is introduced closer to the point of ultimate removal of the "light" phase.

1.2.4 State of the Art

Simkin and Olney (1956) studied liquid-liquid separation in a 95 mm hydrocyclone of conventional design. They examined the effects of geometry and split ratio (Q_o/Q_u) on the separation efficiency of oil and water dispersions. The feed concentration of oil ranged from 25 to 90 vol.%, and the mean diameter of the dispersed phase ranged from 1 to 2 mm. The nominal feed rate was 38 L/min, which gives a Reynolds number based on the feed diameter of over 40,000. Obviously, the liquid drops dispersed in this continuous phase experienced a wide range of turbulent fluctuations, and because the separation efficiency decreased significantly when the volume of the

(a) Oilspin is a registered trademark of Serck Baker, Gloucester, England.
 (b) Vortoil is a registered trademark of BWN, Dandenong, Victoria, Australia.
 (c) Dynaclean is a registered trademark of Alstom, LePont de Claix, France.

hydrocyclone was increased, Simkin and Olney concluded that drop breakup due to turbulence within the hydrocyclone controlled the separation performance rather than drop trajectory and residence time (Figure 1.2).

Unfortunately, because of the high concentrations used in the experiments, most of the experimental data from Simkin's and Olney's study (1958) fall very near the coalescence curves, which makes a clear interpretation of these experiments difficult. Simkin and Olney also concluded that liquid-liquid separation for drop sizes less than 1,000 μm would be ineffective in a hydrocyclone over the range of concentrations studied.

Using a 51 mm hydrocyclone, Burrill and Woods (1970) successfully separated liquid drops of carbon tetrachloride dispersed in water with mean diameters ranging from 150 to 300 μm ($\rho_D > \rho_C$, $\mu_D = \mu_C$). The feed concentration was rather high (12 to 17 vol%); and over a range of split ratios from 4 to 8, Burrill and Woods concluded that a "hindered" discharge mechanism was controlling the separation efficiency. Although the importance of the split ratio on the internal flow structures was apparently not recognized by either Burrill and Woods or by Simkin and Olney, both research groups underscored the significance of making comparison studies between different systems at their individual "optimal" split ratios. For very dilute systems, an "optimal" split ratio induced by hindered discharge conditions is not an important consideration. However, as emphasized by Thew and coworkers (see, especially Colman and Thew 1980) and by Dabir (1983), an optimal ratio of Q_D/Q_U for flooded conditions (no air core) may occur because of changes in the basic flow structure within the core of the hydrocyclone.

For the past 20 years, Thew and his students at Southampton University have pioneered the use of hydrocyclones for separating very dilute suspensions of oil in water ($\rho_D < \rho_C$, $\mu_D = \mu_C$). This extensive development program has been reviewed by Thew (1987). To stabilize the central vortex core region within the hydrocyclone, the Southampton group developed a hydrocyclone with a co-axial withdrawal of liquid through the vortex finder. With this modification, they were able to increase the concentration factor for Kuwait crude ($\rho_D = 0.87 \text{ g/cm}^3$; mean particle size, 41 μm ; flow rate, 60 L/min ; feed concentration, 1,000 ppm) from 20:1 to 160:1 in a 30 mm cylindrical hydrocyclone (Colman and Thew 1980). Many other variations in the geometric scales have appeared since this earlier success and the 8-fold improvement in performance indicated above has been superseded by other designs (see Figure 1.1) that further reduce the turbulence intensity levels as well as stabilize the vortex core.

Thomas, Dabir, and Petty (1984) confirmed and extended the earlier findings of Wallace, Dabir, and Petty (1980) that the centrifugal efficiency of separating kaolinite clay (mean size of 1 μm) in a 10 mm hydrocyclone increases significantly in the presence of Separan AP-30. Flocculation of clay particles certainly occurs in the presence of this polymer, but this phenomenon alone cannot fully explain the results obtained.

In the absence of a particulate phase, Dabir (1983) initiated an experimental study of the effects of polyacrylamide on the secondary flow structures in hydrocyclones. He measured the mean velocity field within a 3"-hydrocyclone operating without an air core. By using a flow visualization technique and a laser doppler anemometer, his results have provided new insights and have raised many interesting questions regarding the flow patterns within a hydrocyclone having the same geometric scales developed earlier by Rietema (1961) for "optimal" performance under solid-liquid separations.

Dabir (1983) also investigated the effect of Separan AP-30 on the core flow in a 3"-hydrocyclone. He concluded that the polymer causes the dampening of velocity fluctuations within the central core region with the result that the shear component of the Reynolds stress has been reduced threefold. Thus, the addition of a high molecular weight polymer in small amounts may provide a novel way to reduce the breakup of oil droplets when finely dispersed oil in water is being separated in a hydrocyclone. This result may also have an important effect on the "sharpness-of-separation" in a classification operation.

1.3 FUTURE CONCEPT DEVELOPMENT

The immediate steps needed to further develop the new centrifugal separator are discussed below, followed by the additional steps needed for the concept's widespread use.

1.3.1 Immediate Steps Required

The concept shown in Figure 1.5 is presently being tested in a prototype vortex chamber. Preliminary results will be presented at the technology fair in May. However, the technical merits of the separation concept as currently perceived should be compared quantitatively with current hydrocyclone technology for de-oiling water (see Figures 1.1 and 1.5).

A comparison study should focus on a specific separation problem such as kerosene in water or vegetable oil in water. The dispersed phase should be dilute ($< 3,000$ wppm), and the mean drop size in the feed should be between 50 to 100 μ m. The effect of flow rate and split ratio on the separation efficiency E_u [see Equation (5)] should be measured for a wide range of feed compositions (1,000 to 3,000 wppm). The laboratory-scale evaluation should be designed for feed rates of commercial interest ($Q_F = 50$ to 100 L/min). The two vortex chambers should be constructed of optically clear material so major differences in flow structure for similar feed rates and split ratios can be observed.

The ability of polymer additives (either polyethylene oxide or polyacrylamide) to reduce droplet breakup and, thereby, increase E_u for both hydrocyclones should be evaluated under similar operating and feed conditions. To minimize the amount of polymer consumed, the feasibility of polymer injection directly into the core region, where the turbulence dissipation rate is highest, should be evaluated for both designs.

Although the new separation concept retains the advantages of no moving parts, the side flow control makes the proposed design more complicated than the Southampton design. We anticipate that this feature can be exploited to increase E_u without a significant power requirement. Obviously, this conjecture must be demonstrated prior to commercial acceptance of this strategy.

1.3.2 Additional Steps Needed for Widespread Use

We have completed two major studies on the hydrodynamics of hydrocyclone flows: one experimental (Dabir 1983) and another theoretical (Chen 1987). The separation concept proposed here (Figure 1.5) stems from insights developed from this earlier research. However, widespread acceptance of turbulent vortex flows as a medium for liquid-liquid separations requires a better understanding of droplet breakup phenomena. The effect of turbulence production rate, the molecular viscosity, surface tension, drop size, and particle concentration on the rate of drop breakup within a turbulent vortex has not been quantified. Fortunately, fundamental studies in this area can now be developed using laser doppler anemometry and in situ particle sizing by laser light scattering. Both of these research tools have appeared since the pioneering and influential work of Simkin and Olney more than thirty years ago.

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2.0 EFFICIENT RECOVERY OF FINELY DIVIDED MINERAL PARTICLES BY CENTRIFUGATION

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ABSTRACT

An efficient recovery of heavy and finely divided mineral particles from light gangue minerals has been investigated by imposing a delicate balance between centrifugal and surface tension forces on these particles.

A mixture of galena and silica fines of 400/500 mesh size was used in this study as a model system. Hydrophobic and heavy galena fines were separated easily from hydrophilic and light silica particles in water/organic liquid under centrifugal force. Better than 90% recovery with 85% purity was possible in a two-liquid system consisting of water and carbon tetrachloride with a centrifugal force less than ten times greater than the force produced by gravity. In the experiments conducted, the effect of surfactant concentration, different organic liquids, angular velocity, amount of organic liquid, and flow rate of slurry on the metallurgical efficiency of upgrading of galena was investigated.

2.1 INTRODUCTION

The fineness of processing plant feed is increasing because of increased mine mechanization. Also, as the grade of ores diminishes, fine grinding is needed to liberate mineral matter before any upgrading operation can occur. Grinding is one of the most energy-intensive processes in mineral processing, consuming tremendous amounts of energy in producing fine particles. Unfortunately, the fine, potentially useful, mineral particles that are produced during the upgrading process and that exist in processing streams are not being recovered. Because of insufficient technology, mineral industries nationally and abroad are losing millions of tons of valuable minerals, such as clay mineral, iron taconite, tin oxide, and tungsten.

Another incentive for removing fine particles is environmental. The removal of suspended solids from mine waste waters and effluent streams of mineral processing plants is a continuing environmental concern. The mineral industries generate more than 78% of the total suspended solid particles produced in the United States. More importantly, however, is the mineral industries' rate of production of suspended solid particles. For example, in 1975 about 47 million tons of suspended solids in mine waste streams were produced, and the projected production in 1985 (based on a 1980 prediction) was 144 million tons. Therefore, an urgent need exists to remove these suspended solid particles efficiently at a reasonable cost.

Numerous suggestions and laboratory-scale attempts have been made to recover such fine minerals by using various processing techniques such as flotation and flocculation. However, only a few of these techniques have proven to be economically viable.

2.2 CONCEPT DESCRIPTION

A major inherent problem in treating fine particles is that their small size makes it extremely difficult to remove fines from the major streams of water flow. As the particles become smaller, density has less effect on the motion of the particles. Consequently, separation of heavy particles from light particles because of gravitational force alone becomes very difficult, if not impossible, for all practical purposes. Therefore, one of the most important factors affecting the upgrading of certain mineral particles is to have the motion of these

particles under control. Some industrial centrifuges can accelerate the motion of particles 60,000 times over that obtained with gravitational force alone. This investigation is aimed at recovering selectively useful, heavy, and hydrophobic mineral particles from light and hydrophilic gangue minerals by using controlled centrifugal forces and by introducing a heavy organic liquid medium.

In this study, centrifugal force is used to control the motion of finely divided particles of less than 37 microns (400 mesh). A preliminary study in our laboratory indicated that it was possible to produce an effective separation of galena particles (specific gravity=7.5) from silica (specific gravity=2.65) using centrifugal forces only two to three times that produced by gravity. The key to this successful separation with such a low centrifugal force is in using the surface properties of these minerals together with an organic heavy liquid. Being a sulfide, galena particles are hydrophobic, while silica particles are hydrophilic.

When the mixture of these two mineral particles is introduced into a centrifuge containing two immiscible liquids--water and heavy organic liquid--hydrophobic particles will pass through water and easily penetrate into the organic phase, while hydrophilic silica particles will not easily cross the interface of the water/organic liquid. However, as the centrifugal force increases, silica particles will also be pulled into the organic phase as long as the density of the organic liquid is less than that of silica. Therefore, a delicate balance exists between gravitational and surface tension forces. Some organic liquids have densities greater than that of silica; however, those liquids are usually too expensive and therefore impractical to use.

A laboratory centrifuge has been used to effect this separation process, as shown in Figure 2.1. A slurry consisting of water and a mixture of two minerals, galena and silica in this study, was introduced into the centrifuge through the feed inlet located in the middle of the centrifuge bowl. The heavy and hydrophobic galena particles reached the water/oil interface earlier than did the light and hydrophilic silica particles. Furthermore, the hydrophobic particles easily penetrated the organic liquid, while the hydrophilic gangue minerals did not. Figure 2.2 shows an industrial-size centrifuge that can be slightly modified and used to effect the separation on a larger scale.

When both the desirable and undesirable particles are hydrophilic, such as scheelite/silica or magnetite/silica, the surface of the desired particles can be modified to be hydrophobic using a surfactant before the above technique is applied.

2.3 EXPERIMENTAL OBSERVATIONS

A slurry consisting of two minerals, a heavy and desirable mineral and a gangue mineral with a predetermined solid concentration, was placed initially in a reservoir tank. A surfactant was added into this tank, when desired. The slurry was then fed at a preset flow rate into a continuously running centrifuge at a given angular velocity ranging from 18 to 300 rad/s (2 g to 640 g). Heavy organic liquid can be introduced continuously near the centrifuge wall through an inlet tube, as indicated in Figure 2.1. However, in this study, a semi-continuous mode of operation was adopted, where a known amount of a heavy organic liquid was placed inside the centrifuge and only slurry was introduced continuously. Salient properties of the heavy liquids chosen for the investigation are listed in Table 2.1.

Galena and silica particles of 400/500 mesh (25 to 37 microns) have been used as a model system. An x-ray diffraction unit was used to analyze the mixture of minerals after the separation process was carried out. All the experiments were conducted at 25 C and at neutral pH. In those experiments, the effect of surfactant concentration, different organic liquids, angular velocity, amount of organic liquid, and flow rate of slurry on the metallurgical efficiency of upgrading of galena was investigated. Each is discussed in the following sections.

FIGURE 2.1. Laboratory Centrifuge Basket

FIGURE 2.2. Industrial Centrifuge Basket

TABLE 2.1. Physical Properties of Heavy Liquids

Liquid	Molecular Weight	Meeting Point (°C)	Boiling Point (°C)	Density (g/cc)
Trichloroethane (CH ₃ CCl ₃)	133.4	-38.4	74.1	1.34
Carbontetrachloride (CCl ₄)	153.82	-23.8	76.8	1.59
Chloroform (CHCl ₃)	119.38	-63.5	61.7	1.48
Tetrabromoethane (CH ₂ BrCBr ₃)	345.67	8.8	112.8	2.87

2.3.1 Effect of Different Heavy Liquids

Five grams each of galena and silica were mixed uniformly in 1500 ml of distilled water, and this slurry was introduced at a rate of 600 ml/min. The angular velocity of the centrifuge was kept constant at 39 rad/s. The amount of heavy organic liquid was kept constant at 250 ml. The results are shown in Table 2.2.

TABLE 2.2. Effect of Different Organic Liquids (a)

	CCl ₄ ^(b)	CCl ₄	CHCl ₃	CH ₃ CCl ₃	CH ₂ BrCBr ₃
Purity (%)	85	68	64	68	67
Recovery (%)	98	98.4	99.1	95.6	38.5

(a) Experimental Conditions: ang. vel.: 39.1 rad/s
 slurry flow rate: 600 ml/min
 slurry conc.: 5 g PbS + 5 g SiO₂
 in 1500 ml water
 amt. of organic liq.: 250 ml

(b) Fresh galena was used. All other samples were kept in water after grinding and exposed to dissolved oxygen in water.

High recovery and grade were obtained when the separation was achieved immediately after grinding. However, because the particle sizes were very small, galena particles were easily oxidized and therefore obtained hydrophilicity after long periods of exposure to dissolved oxygen. Galena was recovered in tetrabromo-ethane because of the organic liquid's high density and an insufficient angular velocity to compensate for the liquid's excessive density.

2.3.2 Effect of Surfactant Concentration

Table 2.3 shows the results of upgrading galena from a mixture of galena and silica as a function of amyl xanthate concentration. In this study, galena particles were oxidized to such an extent that a surfactant had to be added to recover galena. The table shows that as the amount of amyl xanthate added increased, the metallurgical efficiency increased until the amount of the surfactant added exceeded 0.03 lb/ton of slurry.

TABLE 2.3. Effect of Concentration of Amyl Xanthate^(a)

	Amyl Xanthate added (lb/ton of slurry)				
	0	0.01	0.02	0.03	0.04
Purity (%)	0	58	63	68	56
Recovery (%)	0	93	98	98.4	98

(a) Experimental Conditions: ang. vel.: 39.1 rad/s
 slurry flow rate: 600 ml/min
 slurry conc.: 5 g PbS + 5 g SiO₂
 in 1500 ml water
 amt. of organic liq.: 250 ml.

2.3.3 Effect of Angular Velocity

Table 2.4 shows the purity and recovery values of galena when two angular velocities of the centrifuge were used. As expected, the higher the angular velocity reached, the greater the recovery became. However, this occurred at the expense of the grade.

TABLE 2.4. Effect of Angular Velocity^(a)

	Angular Velocity (rad/s)	
	39.1	89
Purity (%)	68	54
Recovery (%)	67	89

(a) Experimental conditions:
 slurry flow rate: 900 ml
 slurry conc.: 5 g PbS + 5 g SiO₂
 in 1500 ml water
 amt. of CCl₄: 250 ml
 amt. xanthate added: 0.03 lb/ton.

2.3.4 Effect of Organic Liquid Added

Table 2.5 shows the metallurgical efficiency of upgrading galena as a function of the amount of CCl₄ added. As the table shows, there is an optimum amount of the heavy organic that should be added. In general, 250 ml of CCl₄ offers the best metallurgical efficiency.

TABLE 2.5. Effect of Organic Liquid Added^(a)

	CCl ₄ added (ml)							
	0	110	150	180	220	250	290	320
Purity (%)	52	54	66	65	67	68	61	51
Recovery (%)	99.5	94	97	96	98	98	84	72

(a) Experimental conditions: ang. vel.: 39 rad/s
 slurry flow rate: 600 ml/min
 slurry conc.: 5 g PbS + 5 g SiO₂ in 1500 ml water
 amt. xanthate added: 0.03 lb/ton.

2.3.5 Effect of Flow Rate of Slurry

The flow rate of slurry introduced into the centrifuge is also important to metallurgical efficiency. Table 2.6 shows that one optimum flow rate offers the best result.

TABLE 2.6. Effect of Slurry Flow Rate^(a)

	Slurry Flow Rate (ml/min)		
	426	686	988
Purity (%)	66	68	68
Recovery (%)	67	98	98

(a) Experimental conditions:

ang. vel.: 39 rad/s
slurry conc.: 5 g PbS + 5 g SiO₂
in 1500 ml water
amt. of CCl₄: 250 ml
amt. of xanthate: 0.03 lb/ton.

2.3.6 Practical Application

The results obtained in this study were based on small-scale semi-batch tests. However, industrial centrifuges are available already in the market to treat fine particle slurry on a larger scale. For example, basket-type centrifuges are manufactured by Centrico, Inc., cylindrical-conical bowl centrifuges and disc centrifuges by Bird Machine Company, Inc., and basket/scroll centrifuges by Tema Systems, Inc. Most of these centrifuges are made to separate oil from water, and, therefore, the speed of rotation is more than what may be required for the current investigation. However, with a little modification, these centrifuges can be used to treat these fine particles. A simple calculation indicates that the cost of treating 5% slurry would be \$4/ton of solids.

2.4 FUTURE CONCEPT DEVELOPMENT

Mineral industries are currently losing many million tons of desirable minerals each year simply because of a lack of technology that can be used to treat fine particles. More than 20% of tungsten ore slimes all over the world, 50% of the tin ore mined in Bolivia, and substantial amounts of taconite ore in the United States are discarded because of a lack of technology.

This study has demonstrated that finely divided heavy and hydrophobic particles can be separated by centrifugal force in a two immiscible liquid system. Further investigations should be carried out on two oxide systems such as scheelite/silica, cassiterite/silica, and iron oxide/silica.

In these systems, because both minerals are originally hydrophilic, a surfactant must be added to make the desirable mineral hydrophobic. For example, hydroxamate or sodium oleate are good examples of such surfactants for these minerals. Further studies pursuing these concepts should be conducted.

A careful study on solid-liquid separation after the separation process should be conducted to make an overall assessment of the process. We conducted a preliminary investigation on the separation of minerals from the organic phase and found that more than 90% of organic liquid can be recovered and reused without distillation. Further investigation along this line should be carried out.

2.5 LITERATURE SURVEY

No literature information is available relating directly to the concept used in this study. However, the fluid behavior in a centrifuge has been well documented (Coulson and Richardson 1978; Hsu 1981; Svarovsky 1977). Many investigations have concerned separation of mineral particles using two immiscible liquids. Prudich and

Henry (1978) have attempted to separate coal particles from gangue minerals by an oil/water system. Other investigators have developed force balances between gravity and surface tension on particles placed in liquid (Maru, Wasan and Kintner 1971; Winitzer 1973; Huh and Mason; Rapachietta and Neumann 1977). Others have attempted to separate particles by liquid-liquid contacting (Albertason 1971; Raghavan and Fuerstenau 1975).

The literature survey reveals a need to develop a fundamental approach to particle behavior in two immiscible liquid systems under the influence of centrifugal force.

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BIOTECHNOLOGY SEPARATIONS

3.0 BIOTECHNOLOGY SEPARATION OF PYRITE FROM COAL

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ABSTRACT

The use of microorganisms, particularly lithotrophic bacteria such as Thiobacillus (T.) ferrooxidans, was investigated as a cost-effective method for recovering coal that is currently discarded as being too dirty to burn. The bacteria are used to modify the surfaces of the pyrite particles contained in the sulfur. By altering the surface of the pyrite, it can be separated from the coal by the froth flotation process, a separation that would not be possible without pretreatment.

Experiments were conducted using two strains of lithotrophic bacteria, three species of nonlithotrophic bacteria, and one species of yeast. Results indicate that, while all microorganisms showed considerable ability to alter the pyrite surface and thus prevent flotation, the most effective was one of the strains of T. ferrooxidans, which produced nearly complete suppression. The tests also determined that the suppression is caused by direct cellular attachment and the action of intracellular enzymes, not by extracellular enzymes released into solution.

3.1 INTRODUCTION

In most coal mines, 20% or more of the mined coal consists of material that is finer than 0.5 millimeters and contains large amounts of ash and sulfur. Because of the difficulty of cleaning this fine coal, it is frequently discarded. Therefore, much of the heating value of the coal is lost because of a lack of a sufficiently effective cleaning technique.

Bacteria and other microorganisms provide a promising way to improve the efficiency of processing coal and other minerals. Because bacteria apply biotic energy in materials cycling, replacing fuel, microorganisms can be considered as the equivalent of energy (Decker 1985). Also, using bacteria can provide opportunities for reducing capital and labor costs. Applying bacterial techniques to fine coal processing could not only save energy, but could also improve cleaning efficiency enough to allow coals currently considered to be too dirty to burn to be recovered and used.

Bacteria have long been known to be able to leach impurities such as pyrite from coal, thus reducing the sulfur content. However, no coal preparation plants use bacteria in their processes, largely because of two factors: 1) pyrite leaching by bacterially catalyzed dissolution is fairly slow, and 2) pyrite leaching processes do not reduce the coal ash content. Therefore, an unconventional application of bacteria in mineral processing is needed.

3.2 CONCEPT ASSESSMENT

In the following sections, the concept is described, and its potential energy savings, technical feasibility, and status are discussed.

3.2.1 Concept Description

The proposed concept uses bacteria and bacterial enzymes to alter the surface of the pyrite particles in coal. This surface alteration occurs very rapidly and allows the coal to be removed from the pyrite by froth

flotation. If the pyrite surface is not altered, the performance of froth flotation in removing pyrite, and therefore in reducing sulfur, is poor.

Froth flotation is based on the preferential attachment of air bubbles to surfaces that are hydrophobic, or have low affinity for water. When air is dispersed in a mixture of finely ground minerals in water, the hydrophobic particles attach to the air bubbles and are carried to the surface, leaving the hydrophilic, or water-loving, minerals behind. Various reagents are added to adjust the surface chemistry of the mineral particles and to alter the properties of the mineral-laden froth on the surface, therefore affecting the performance of the process. This technique is particularly suitable for coal because coal surfaces are naturally hydrophobic, whereas most of the associated minerals are hydrophilic (Aplan 1978).

The major drawback to using froth flotation for cleaning fine coal particles is that, unlike other minerals in coal, pyrite is naturally hydrophobic. Pyrite is therefore floated along with the coal, increasing the sulfur content of the froth product. This problem increases as the pyrite particles become smaller because the pyrite's density is not able to keep the pyrite from floating. The only solution is to selectively alter the surface of the pyrite particles from hydrophobic to hydrophilic, thus preventing their flotation, but without adversely affecting the hydrophobicity of the coal.

Lithotrophic ("rock-eating") bacteria such as T. ferrooxidans will catalyze the oxidation of pyrite to a soluble form. While complete dissolution of the pyrite requires several weeks, the bacteria attach to and alter the pyrite surface in a matter of minutes. This alteration was predicted to change the pyrite surface from hydrophobic to hydrophilic, thus allowing the froth flotation process to float the coal away from the pyrite.

Experiments were conducted at Michigan Technological University (MTU) to test the ability of bacteria to reduce the tendency of pyrite to float. The results are shown in Table 3.1. In the experiments, pure pyrite at pH=2 was used. In addition to two strains of T. ferrooxidans, three other species of unrelated bacteria (Pseudomonas fluorescens, Klebsiella terrigena, and Lactobacillus acidophilus), and one species of yeast (Saccharomyces cerevisiae) were used. In the table, the lowered values of the percentage of pyrite floating indicate that the efficiency of the pyrite depression has increased.

The experiments at MTU showed that, while live cultures of T. ferrooxidans are most effective for depressing the flotation of pyrite, other bacteria also exhibit the ability to reduce (depress) pyrite flotation, even if the bacteria have no specific capability to dissolve pyrite. The depression is therefore at least partly the result of the pyrite particles becoming coated by microbial proteins. In addition to the generic action, T. ferrooxidans specifically attach to and oxidize the pyrite surface, thus producing a more effective depression

TABLE 3.1. Results of Bacterial Depression Tests Conducted at MTU

<u>Microorganism Used</u>	<u>Percentage of Pyrite Floating</u> <u>(mean value for all tests)</u>
Controls, No microorganisms	21.8 ± 2.1%
<u>T. ferrooxidans</u>	6.78 ± 0.07%
<u>T. ferrooxidans</u> , strain PA1	2.48 ± 0.06%
<u>Pseudomonas fluorescens</u>	5.4 ± 1.5%
<u>Klebsiella terrigena</u>	4.5 ± 0.2%
<u>Lactobacillus acidophilus</u>	7.0 ± 0.5%
<u>Saccharomyces cerevisiae</u>	2.5 ± 0.3%

of the pyrite. The pyrite is oxidized by intracellular enzymes that are not released into the suspending media, so either whole bacteria or bacterial extracts are needed for this process.

The proposed process would be conducted in three stages using a bacterial culture tank, a conditioner, and a froth flotation tank. Bacteria would be cultured in the culture tank, using high-sulfur coal tailings and small quantities of trace minerals as bacterial nutrients. The cultured bacteria would then be added to the conditioning tank, along with the coal to be processed, and mixed for a short period to allow the bacteria to completely attach to the pyrite. The pyrite and ash minerals would then be removed in the froth flotation stage, leaving a clean, low-ash, fine coal product that could be burned to produce power with minimal emission control.

The optimum conditions for the coal flotation solution, such as pH and reagent dosage, vary greatly for coals obtained from various seams. In many cases, the solution conditions will not allow living cultures of T. ferrooxidans to be used because they will be rapidly killed by high pH values. In those cases, two options are available. Either the relevant enzymes can be extracted from the bacterial culture and added to the conditioner in the absence of living cells, or a culture of bacteria that can tolerate the solution conditions can be used. These modifications will allow the process to be applied to nearly all coals that can be made to meet sulfur standards by the removal of pyritic sulfur.

3.2.2 Potential Energy Savings

The bacterially enhanced flotation process will recover the heating value that would otherwise be lost, without adversely affecting the environment. With little additional expenditure of processing energy and capital, delivered heating value of the mine product can be increased by 20%. Overall environmental impact may actually be reduced because less coal would have to be mined if 20% were not discarded.

Unlike many other processes for coal desulfurization, the proposed process does not use expensive or dangerous chemicals, and the waste is in a solid form that can easily be disposed of. The largest nonconventional requirement is the bacterial culture tank. However, the feed for this culture tank can be supplied from by-products of the cleaning plant; therefore, the tank is quite inexpensive to operate.

3.2.3 Technical Feasibility

Experiments conducted to date have used pyrite mined from pure deposits of the mineral. Using that type of pyrite, bacteria are very effective for suppressing flotation. However, the pyrite actually contained in coal appears to have different surface properties because of its formation and long residence in the presence of complex organic molecules. Flotation of coal pyrite is therefore more difficult to prevent than is flotation of pure mineral pyrite. Further work is needed to improve the effectiveness of depressing coal pyrite by bacteria. The effectiveness can be improved by adjusting the treatment time and solution conditions.

The bacterially enhanced flotation process may be useful for all coals that are currently too high in pyritic sulfur to meet EPA standards. For example, in some cases coals that currently are suitable only for power generation may be sufficiently upgraded for use as higher-value metallurgical coal. Also, this process could be used in small portable plants to process coal waste dumps and therefore recover usable coal without the expense and high energy consumption of mining.

Coals containing substantial amounts of organic sulfur will also be improved by this process but will be primarily suitable as "blend products" that can be used with low-sulfur coals, or to remove part of the load from power plant stack-gas scrubbers. Coals that are very high in organic sulfur (3%) cannot be sufficiently desulfurized by any known, economically practical process. Coals lacking natural hydrophobicity cannot be treated by the proposed process.

A process related to the proposed concept could be applied to the leaching of precious metals from refractory ores. Precious metals often occur as finely divided particles dispersed in a pyrite-rich matrix. To treat these ores by cyanide leaching, the rock must be ground until the precious metal inclusions are exposed to the cyanide

solution. This requires tremendous amounts of energy because grinding is a very inefficient process. However, if T. ferrooxidans were used to lightly leach the pyrite matrix, the porosity of the rock would increase sufficiently to make extensive grinding unnecessary. A great deal of energy would be saved because bacterial leaching is a spontaneous process that does not require any external energy inputs. Bacterial pretreatment is potentially of great use to the precious metals industry as well.

3.2.4 State-of-the-Art

Several physical and chemical techniques have been investigated for cleaning and desulfurizing coal wastes. However, the physical separation of coal and pyrite usually is not sufficiently selective at fine sizes, and chemical techniques tend to be expensive and often produce toxic waste products that are difficult to dispose of. Most interest has concentrated on developing physical separations with improved selectivity because such processes have low enough costs to be useful (Kawatra and Eisele 1987).

Because purely physical separations appear to be approaching their ultimate limits for removing sulfur from coal, other technology is needed to achieve further improvements. Biological processing, which possesses many of the advantages of chemical processing at less expense, is a promising method for achieving these improvements (Kawatra, Eisele and Bagley 1987).

The most widely investigated application of bacteria to mineral processing is as catalysts for leaching operations. The bacteria increase the rate of dissolution processes, which normally occur very slowly, such as oxidizing and dissolving pyrite in acid solutions. Pyrite dissolution is accelerated several hundred-fold by the action of bacteria such as T. ferrooxidans and Sulfolobus (S.) acidocaldarius (Ehrlich 1988). These bacteria have therefore been extensively investigated for leaching pyritic sulfur from coal. However, complete leaching of pyrite by T. ferrooxidans typically requires several weeks (Hoffmann et al. 1981), and the high-temperature organism S. acidocaldarius, while more rapid, still requires processing times of about one week (Kargi and Robinson 1985).

The large capital investment required for a leaching tank of sufficient volume makes coal desulfurization by bacterial leaching impractical at current coal prices. Work conducted at MTU has shown that intense aeration shortens the necessary leaching time by several days, but the process is still too slow to be economical.

Kepton et al. (1988) discovered that conditioning very high sulfur coals with T. ferrooxidans improved the ability of oil agglomeration to remove pyrite from the coal. Unfortunately, oil agglomeration is not a particularly economical process because of the cost of the large amounts of oil used. However, the phenomena responsible for the performance of oil agglomeration are similar to those involved in froth flotation, so the bacterial pretreatment that was successful for oil agglomeration is equally applicable to froth flotation (Attia and Elzeky 1985; Dogan et al. 1985). The major barrier to applying this process remains the peculiar characteristics of coal pyrite relative to pure mineral pyrite, which makes depression of the coal pyrite in flotation more difficult than would be expected.

Various chemicals have been found in the past to depress the flotation of pyrite (Baker and Miller 1971). However, these chemicals also depress the flotation of coal to some extent, which is not true for bacterial pyrite depression, and are no more effective for depressing pyrite than is the bacterial method. The bacterially assisted process therefore is superior to existing techniques.

3.3 FUTURE CONCEPT DEVELOPMENT

The most immediate step required to further develop the concept is to improve the effectiveness of bacterial depression of coal pyrite. Improving the effectiveness will involve using a modified conditioning technique, consisting of vigorous, forced aeration at high bacteria and solids concentrations. Also, the salts in solution will be adjusted to the optimum concentrations determined in earlier leaching experiments. Using this modified

conditioning technique will allow the pyrite to be more strongly depressed in the froth flotation stage. This also will preferentially dissolve the extremely fine pyrite inclusions that are difficult to physically separate from coal. Further work is also needed to develop bacterial pretreatment of refractory precious metal ores to reduce grinding costs.

After the laboratory test work has been completed, a small pilot circuit that uses bacterially assisted flotation will be designed and constructed. Samples of fine coal currently being discarded from various plants because of high sulfur content will be collected, and the pilot circuit's capability to treat these coals will be determined. When the pilot tests have been completed, arrangements will be made with a coal cleaning operation to treat either a coal waste dump or a plant waste stream using the pilot circuit, as a final test of the concept.

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4.0 PERIODIC, CROSS-FLOW SEPARATION OF LARGE MOLECULES, ESPECIALLY PROTEINS, ACCORDING TO THEIR DIFFUSION COEFFICIENTS

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ABSTRACT

A method is being developed for separating relatively large molecules that have different diffusion coefficients. The molecules, in solution in their natural solvent environment, are separated by two mutually perpendicular coordinated flows, both periodic and bi-directional. The molecules are subjected to only gentle shear. More rapidly diffusing species concentrate at one end of a separator tube, while more slowly diffusing species concentrate at the other end. The cut point is continuously adjustable without requiring hardware changes, as is the tradeoff between sharpness of separation and production rate. Sharp separations of molecules having slightly different diffusion coefficients are possible. The new method can be viewed as a combination of field flow fractionation and parametric pumping.

The new concept is potentially attractive for separating mixtures of delicate biochemicals, and hazardous or expensive inorganics. The anticipated rapid growth of pharmaceutical proteins produced by recombinant DNA technology provides a prime potential market. Other possible markets are flavors and fragrances, and expensive or hazardous inorganics such as those found in nuclear fuel reprocessing.

A mathematical model was developed and used to predict the performance of the method on a binary mixture of proteins in aqueous solution. The proteins are assumed to have molecular diffusion coefficients of 0.9×10^{-7} and 1.0×10^{-7} cm²/s. Separation is calculated to occur in 1 hour with recoveries and purities exceeding 99%. Calculations indicate that higher recoveries and purities may be readily achieved with somewhat more processing time; for example, 99.8% recovery and purity would require 2 hours of processing time. The feed protein concentration is approximately 0.4% w and the rate of processing is about 1 gram of protein per liter of separator tube volume per hour.

The next logical steps in developing this concept are to use the mathematical model to explore a wide range of operating conditions. Also, the new process should be discussed with pharmaceutical and possibly other companies and with equipment manufacturers. If these contacts are encouraging, the method should be explored further with laboratory-scale proof-of-principle experiments and then production-scale experiments.

4.1 CONCEPT ASSESSMENT

This section includes a description of the concept, and discussions of the concept's potential energy savings, technical feasibility, and present status.

4.1.1 Description of the Concept

This concept involves a method for separating large molecules with different diffusion coefficients. The separation is caused by the coordination of two types of mutually perpendicular, coordinated periodic flows that are bi-directional. A periodic cross-flow produces short-range, time-varying partial separations, and a periodic axial flow multiplies and converts the short-range separations into useful separations in the axial direction. The molecules, in solution in a low molecular weight solvent, are processed in a tube of rectangular cross section. Two parallel walls consist of membranes that are permeable to the solvent but not to the molecules being separated. The other two walls are completely impermeable, and the ends of the tubes are alternately inlets and outlets for axial flow.

The method is inherently very flexible. The number of separation stages within a single tube can be varied from a few to many hundreds without hardware modifications; the change is made simply by varying user-controlled operating parameters. Both batch and continuous operation are feasible. The molecules that diffuse more slowly are concentrated and removed from one end of the tube, while the molecules that diffuse more rapidly are concentrated and removed at the other end of the tube. Alternatively, the method can be operated in a chromatographic mode where molecules emerge at one end of the tube sequentially in the order of their molecular diffusion coefficient values.

The concept can be viewed as a successful combination of field flow fractionation (Giddings et al. 1986; Janca 1988) and parametric pumping (Wilhelm et al. 1988). Many of the best features of those processes are captured, and the less desirable features are avoided.

Molecules are processed in their natural solvent environments and are subjected only to very gentle shear. The delicate chemicals and biochemicals should not be harmed. The process may be especially helpful for such types of molecules as proteins, enzymes, macromolecules, flavors, fragrances, and costly or environmentally hazardous inorganics. No temperature, pH, ionic strength, or other intensive variable changes are required in this separation process (except modest pressure variations for driving the flows). Waste streams are not generated because no reagents or separating agents are added.

Figures 4.1 and 4.2 help explain the concept. Figure 4.1 shows the hardware used and Figure 4.2 explains a batch separation sequence. Each is discussed in more detail in the following subsections, followed by general discussions of the proposed process operated in continuous and chromatographic modes.

Schematic of Hardware

Figure 4.1 is a schematic of a laboratory batch version; the center section, drawn with thick lines, comprises the separator tube and associated chambers, all of rectangular cross section. The two horizontal dashed lines represent membrane sheets that form two parallel walls of the separator tube 2. These membranes are perpendicular to the plane of the drawing. The other two walls of the tube (parallel to the plane of the drawing) are impermeable. The ends of the tube adjacent to A and B are open and permit inflow and outflow.

The separator tube 2 is long and thin. Its dimensions are typically a few centimeters in the A, B direction; much less than 1 mm in the C, D direction; and a few centimeters in the direction perpendicular to the plane of the drawing. Auxiliary chambers 1 and 3 are adjacent to the main separator tube.

The auxiliary equipment surrounding the separator tube and associated chambers consists of four syringes A,B,C,D; small-bore connecting tubing (not labeled); and on-off valves a,b,c,...,p for connecting the syringes to different parts of the separator tube 2 and associated chambers 1 and 3. Syringes A and B can produce axial flow of solution through the separator tube, while syringes C and D allow the cross-flow of solvent through the membrane walls.

Sequence of Operations Comprising a Cycle

Figure 4.2 focuses on the separator tube 2 of Figure 4.1 and shows a sequence of six steps comprising a cycle that is repeated indefinitely to bring about the separation. For clarity, a batch separation of two species in solution is described; generalizations are discussed later. Each of the six lines in Figure 4.2 shows the action taken during a step and the state resulting from the action, i.e., the state resulting at the end of the step.

The separator tube 2 is filled initially with a solution of uniform composition containing two species, F and S. For this example, F will be the faster diffusing species, and S the slower diffusing species. The steps to be described concentrate F at the end of the tube adjacent to A and simultaneously concentrate S at the end of the tube adjacent to B.

FIGURE 4.1. Schematic of the Concept

Step 1 involves a cross-flow of solvent into separator tube 2 through the upper membrane, across the tube, and out through the lower membrane. This cross-flow of solvent originates from syringe C and flows through valves f and g into auxiliary chamber 1. It then flows through the upper membrane, across separator tube 2, through the lower membrane, into auxiliary chamber 3, through valves n and o, and into syringe D. The cross-flow convects F and S molecules in the separator tube to the inner surface of the lower membrane wall, establishing a thin superimposed layer of concentrated F and S molecules immediately adjacent to the membrane.

Step 2 involves an immediate and rapid flow of pure fluid toward B. The F and S molecules do not move appreciably because they are still positioned in a thin boundary layer adjacent to the lower membrane. The average distance the fluid is moved, x_2 , is selected to achieve a zero net flow of fluid over the cycle.

Step 3 is a quiescent period during which no flow occurs. The duration of step 3 is selected to allow the concentration polarization of both species established during step 1 and remaining at the end of step 2 to relax partially by molecular diffusion perpendicular to the membrane wall. At the end of step 3, the molecules are in two partially superimposed layers, one containing F and the other containing S molecules. The F layer is thicker than the S layer; that is, the F layer extends farther from the membrane surface into the tube than the S layer because the diffusion coefficient for F is greater than it is for S. If the initial concentration polarization layer is much thinner than the thickness of the separator tube, then the diffused layer thicknesses are proportional to the square roots of their respective molecular diffusivities. If the initial layer thicknesses are appreciable, a more complicated analytical relationship exists.

In step 4, a fast but laminar axial flow in the direction of B to A displaces a small fraction of the fluid in the tube in a relatively short time before additional molecular diffusion occurs. Because the axial flow is laminar, it typically moves the F molecules farther than the S molecules since the F molecules typically extend farther into the tube cross-section than do the S molecules. Let x_4 be the average axial displacement of the

FIGURE 4.2. A Batch Separation Sequence

fluid, x_{4F} be the average axial displacement of the F molecules, and x_{4S} be the average axial displacement of the S molecules. All of these displacements are negative because the flow is toward A. From the above considerations, $x_4 < x_{4F} < x_{4S}$. The second of these inequalities, $x_{4F} < x_{4S}$, represents some separation in the axial direction. The separation distance $|x_{4F} - x_{4S}|$ in the axial direction is proportional to the fluid displacement x_4 .

Step 5 consists of a fast downward cross-flow to re-establish the concentration polarization present at the end of steps 1 and 2. This downward cross-flow is followed by fast upward cross-flow to convect the layer of concentrated F and S molecules to a plane midway between the two membrane walls.

In step 6, fast axial flow in the direction A to B through the separator tube displaces a small fraction of the fluid in the tube. This sixth step moves both the F and S molecules toward B by the same distance, say x_6 .

Over a cycle comprising these six steps, the average axial positions of the F molecules and the S molecules are controlled by the axial displacements in steps 4 and 6. Because the displacements x_{4F} and x_{4S} are proportional to x_4 , the magnitude of x_4 determines the separation distance $|x_{4F} - x_{4S}|$. Further specification of x_6 determines

the direction of motion of the F and the S molecules. If, for example, we choose $x_8 = -(x_{4F} + x_{4S})/2$, then the average distance the F molecules move toward A is $|(x_{4F} - x_{4S})/2|$ and the average distance the S molecules move toward B is the same distance $|(x_{4F} - x_{4S})/2|$.

To have a zero net flow of fluid over the cycle comprising steps 1 through 6, x_2 is selected to satisfy $x_2 + x_4 + x_8 = 0$. Thus, over the six-step cycle, F molecules move, on the average, a distance $|(x_{4F} - x_{4S})/2|$ toward A; S molecules move the same distance toward B; and the net flow of fluid is zero.

Although the separation produced by the above cycle is modest, repeating the cycle many times can result in a sharp separation with F molecules at the A end of the separator tube and S molecules at the B end.

Chromatographic Operation

The separation can also be done in a chromatographic mode, for example, by selecting the displacement x_8 in step 8 such that both species move toward B. The necessary condition is $x_8 = k|x_{4F}|$, where $1 < k < \text{infinity}$. As $k \rightarrow \text{infinity}$, the time of the chromatographic process becomes short, but the separation between the F and S pulses degrades. As $k \rightarrow 1$, the time of the chromatographic process grows without bound, but the separation between the F and S pulses also increases without bound. In the above chromatographic operation, the slower diffusing species S emerges first.

The previous examples were both batch mode and described separation of molecules of two species. The process will actually be applied in a continuous mode and can be used sequentially in several continuous separations to separate mixtures of molecules having more than two sizes.

Continuous Operation

Continuous operation can easily be achieved by introducing the feed steadily or discretely into the separator tube at an intermediate axial position, preferably where the tube and feed concentrations match most closely, and withdrawing product streams simultaneously from syringes A and B.

Multicomponent Mixtures

In the batch mode, a logical extension for multicomponent mixtures is to concentrate and remove the species one at a time in the reverse order of the magnitudes of their diffusion coefficients. However, in the continuous mode, the separation splits the feed stream into two streams and several separate separations would be required. The cut point is controlled by the selection of the axial flows. Species with diffusivities greater than the cut-point diffusivity migrate toward A, and the species with diffusivities lower than the cut-point diffusivity migrate toward B.

4.1.2 Potential Energy Savings and Other Benefits

A likely growth area over the next several decades in the United States, Japan, and Western Europe is biochemicals, especially therapeutic high value proteins produced using recombinant DNA approaches. A wide variety of products are under laboratory development, and product values from this new industry are estimated to total several tens of billions of dollars annually by the year 2000. Examples products include human insulin, human growth hormone, interleukin anticancer agents, interferons for cancer and viral infections, and super oxide dismutase for limiting heart damage to blood driving reperfusion after heart attacks.

One of these products, human insulin, is already being produced on a large scale in the United States by Eli Lilly Company using human genes in *E. coli* bacteria. Thirty-one steps of separation and purification are involved. The cost in capital, losses of product, consumed reagents, chromatographic packings, and other adsorbents is considerable. Of great importance is the yield per step. For example, a yield of 98% per separation step when applied to 31 steps in series produces an overall yield of only 3.8%. All of these losses and operating costs translate into significant amounts of wasted energy.

If the proposed process is developed, it could dramatically reduce the cost of separations in a growing industry where separations loom as a major operating cost. Saving capital and operating costs, especially in consumable reagents and supplies, and increasing yields can reduce energy consumption. While estimating is difficult, we believe savings from \$1 to \$10 billion per year are feasible by the year 2000. Engineering contributions of the type proposed here are essential to the international competitiveness of the U.S. biochemical industry as it develops recombinant DNA products.

A similar but smaller market is the flavors and fragrances industry. The process may also be desirable for separating inorganic salts that are unusually valuable or hazardous, as in nuclear fuel reprocessing.

4.1.3 Technical Feasibility and Impediments to Wide-Scale Use

Because the proposed method of separation has only recently been conceived, its theoretical and practical characteristics are unknown. To date, a conceptual base has been established, and a theoretical analysis has been conducted based on reasonable mathematical modeling. Yet to be done are the practical design, implementation, proof-of-principle experiments, experimental evaluation of process characteristics, and determination of the most promising classes of uses.

An approximate mathematical model for the batch version of the process has been developed. Each of the six steps in a cycle have been described by classical equations free of unknown or adjustable parameters. Although space limitations do not allow the model to be presented here, the model has been used to evaluate the effects of equipment dimensions and modes of operation on performance.

Table 4.1 provides selected simulation results for an equimolar binary mixture of proteins with diffusion coefficients 0.9×10^{-7} and 1.0×10^{-7} cm²/s. The table describes how a process with a separator tube thickness, d , and length, L , will perform given that the purity ratio, R_p , is attained at both ends of the separator tube and that relaxation time, t_3 , is allowed in step 3. These calculation results are discussed in the following subsections along with consideration of Starling flow, scaleup, and the implications of the approval policies of the Food and Drug Administration (FDA).

Cycle and Separation Time

The cycle time, T , in Table 4.1 is the total time of a six-step cycle. The relaxation time, t_3 , accounts for most of the cycle time. The product of the cycle time and the number of cycles, N , is the total time required for the separation, or the residence time. The residence time is the ratio of the separator tube volume to the volumetric flow rate of the feed.

To achieve short cycle times, the relaxation time, t_3 , must be short. This relaxation time is controlled by 1) the molecular diffusion coefficients of the proteins, assumed here to be about 10^{-7} cm²/s, 2) the thickness of the diffused layer present at the end of step 3, and 3) the ratio of the diffused layer thickness to the polarized layer thickness present at the end of steps 1 and 2. This ratio must be about 2 or more to achieve a reasonable separation per cycle. If the desired relaxation time is about 1 second, the above constraints indicate a polarized layer thickness of about 2×10^{-4} .

Sharpness of Separation

Very sharp separations with high purities of both products are feasible. In Table 4.1, the processing requirements for purity ratios of 100, 200, and 500 are given. This purity ratio, R_p , is the ratio of the concentrations of species F to S in the F-rich product stream (tube end A) and also the ratio of the concentrations of S to F in the S-rich product (tube end B). Symmetrical separation has been required to ensure high product recovery as well as high product purity.

TABLE 4.1. Simulation Results

R_p	t_3	d	L	x_4	T	N	τ	Q	C_f	$\dot{m}$	$\dot{m}/V_{\text{tube}}$
100	1	0.001	100	1.20	1.16	2988	3463	10.4	0.040	416	41.6
100	1	0.01	100	3.41	1.18	2983	3523	102.2	0.004	409	4.09
100	1	0.02	100	6.55	1.21	2987	3622	198.8	0.002	398	1.99
100	1	0.03	100	9.70	1.24	2988	3716	290.6	0.0013	388	1.29
100	1	0.04	100	12.85	1.28	2988	3811	377.9	0.001	378	0.94
100	1	0.05	100	16.00	1.31	2989	3906	460.9	0.0008	369	0.74
100	1	0.10	100	31.80	1.47	2985	4394	823.3	0.0004	329	0.33
200	1	0.03	100	8.44	1.23	3434	4225	255.6	0.0013	341	1.14
200	2	0.03	100	6.34	2.21	3209	7090	152.3	0.0013	203	0.68
100	2	0.03	100	7.29	2.22	2791	6195	174.3	0.0013	232	0.77
500	1	0.03	100	7.19	1.22	4031	4905	220.2	0.0013	294	0.98
500	1.5	0.05	100	10.05	1.75	3853	6726	267.6	0.0008	214	0.43

Nomenclature

R_p	Purity ratio. The ratio of the concentration of species F to that of species S at tube end
A	dimensionless
t_3	Time allowed in step 3 for partial relaxation of the concentration polarization, sec.
d	The thickness of the separator tube, cm
L	The length of the separator tube, cm
T	Time required for one cycle of six steps, sec.
N	Number of cycles required to achieve specified separation, dimensionless
τ	Residence time. The ratio of the separator tube volume to the volumetric feed rate, sec.
Q	Volumetric feed rate, cm ³ /hr
C_f	Fractional total protein concentration in the feed
$\dot{m}$	Total mass flow rate of both proteins, mg/hr.
$\dot{m}/V_{\text{tube}}$	Total mass flow rate of proteins through the system divided by the volume of the separator tube mg/hr-cm ³
x_4	The average distance which the bulk fluid is moved in step 4.

Lines 4, 8, and 11 in Table 4.1 show that high purity ratios can be achieved with reasonable processing times. The processing time for a purity ratio of 100 is 62 minutes. The processing times for purity ratios of 200 and 500 are 72 and 112 minutes, respectively.

Maximum Feed Protein Concentrations

The maximum concentration of protein that is practical in the feed is not known precisely at this time, but an order-of-magnitude estimate is 0.1% to 1.0%. This estimate is based on considering the maximum thickness that is reasonable in the polarized protein layer at the inner surface of the lower membrane at the end of step 1 and the maximum practical concentration of protein in that layer. We estimate that the thickness of the polarized layer should not exceed 2% or 3% of tube thickness so that the diffused layer present at the end of step 3 can be several times thicker but still not project beyond 10% to 20% of the tube width.

The maximum concentration of protein in the polarized layer is probably from 10% to 50% in order to avoid blocking the cross-flow through the membrane. Assuming 2% of tube thickness for the layer thickness and 20% for the concentration of protein in the polarized layer implies a feed protein concentration of 0.4%. We therefore estimate that the maximum feed protein concentration is likely to range from 0.1% to 1.0%. This maximum feed protein concentration is based on a tube thickness of 0.01 cm. This maximum is inversely proportional to tube thickness. Therefore, thicker separation tubes require more dilute feed.

Rates of Production

A meaningful criterion for comparing rates of production is the quantity $\dot{m}/V_{\text{tube}}$ in the last column of Table 4.1, the mass of protein processed per unit time per unit volume of separator tube. This quantity depends

most strongly on d , the tube thickness. As the tube thickness is increased, the concentration of protein in the feed must be decreased in order to limit the protein concentration in the polarized layer at the end of steps 1 and 2. The reasoning for this limitation is discussed above in "Maximum Feed Protein Concentrations." Thus, although a thicker tube can process a greater volume of feed per unit time, the mass of protein processed per unit time does not increase.

Starling Flow

The axial flows in steps 2, 4, and 6 of the six-step cycle have associated axial pressure gradients. These pressure gradients also cause what is called Starling flow through the membrane walls. In the upstream half of the tube the Starling flow leaves the separator tube 2 and enters chambers 1 and 3 (Figure 4.1). In the downstream half of the tube, the Starling flow returns from chambers 1 and 3 into separator tube 2. Starling flow is undesirable because it degrades the separation.

Starling flow can be eliminated by flowing fluid through chambers 1 and 3 at the rate that causes the same pressure gradient along these chambers as exists in the separator tube.

Scaleup

As already discussed in "Rates of Production," the processing capacity per tube does not increase by increasing the thickness, d , of the separator tube. Therefore, scaleup is best accomplished by simply stacking separator tubes in parallel. The stacking arrangement automatically eliminates Starling flow in the interior tubes and conveniently enables the cross-flow to pass through the tubes in series.

Although the simulation results in Table 4.1 show a higher production rate per unit volume of separator tube for thinner tubes, there are practical lower limits on thickness. However, little loss in production rate occurs per tube when thickness is increased. Therefore, the choice of separator tube thickness is governed by practical mechanical considerations. The thinnest tube possible should be used, in both laboratory and production-scale equipment, to minimize the total tube volume and to maximize the feed protein concentration.

Implications of FDA Approval Practices

When the FDA approves a drug, the approval normally encompasses not only the drug's composition, but its method of manufacture, including separation and purification methods. What is approved are the reaction, separation and purification methods used in the laboratory to manufacture the drug samples tested in the field. Later improvements in separation and purification methods cannot be adopted unless costly new field tests are performed. In practice, the methods first used in the laboratory tend to become the production methods.

Therefore, attractiveness and widespread use as a laboratory method are important positive factors in promoting a separation and purification method for production. The proposed process has characteristics that make it attractive for both laboratory and production uses. In the laboratory, flexibility, speed, and a high degree of resolution are desirable characteristics. The proposed method retains all of these attributes and is easily scaled up by stacking many laboratory size tubes in a sandwich arrangement as discussed in the previous subsection.

4.1.4 Current Status and Competing Technologies

The methods of separation and purification used and presently planned for the recombinant DNA industry are often scaledup versions of laboratory separation methods. Very prominent are centrifugation, precipitation, extraction, adsorption, ultrafiltration, and chromatographic separations. In the latter stages of separation very specific adsorbents, based on monoclonal antibodies, are used if the cost in dollars and time required to develop them are permissible. In addition to these existing methods, we believe that significant research efforts are under way in the areas of electrophoresis and affinity chromatography.

4.2 DEVELOPMENT PROGRAM

Two urgent steps need to be taken for the future development of the concept: 1) use the mathematical model to explore more completely feasible ranges of design and operating conditions and 2) discuss the new process with pharmaceutical companies and equipment manufacturers. Additional steps that are needed to implement widespread use of the concept are as follows:

- design and build laboratory-scale apparatus
- perform proof-of-principle experiments on a representative binary protein mixture
- refine and validate the mathematical model
- evaluate and compare the new method against competing technologies for laboratory analysis applications
- design and build a prototype production-scale apparatus
- test and refine the production-scale apparatus
- evaluate and compare the new method against competing technologies for production-scale applications
- compare economics with current and potential future technologies
- establish suppliers and marketers of laboratory and production-scale equipment
- provide technical support and monitor progress.

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The present study was designed to provide information on the effects of the following factors on the growth and development of the chick: (1) the effect of the type of feed, (2) the effect of the type of housing, (3) the effect of the type of lighting, and (4) the effect of the type of ventilation.

- 1. The effect of the type of feed on the growth and development of the chick.
- 2. The effect of the type of housing on the growth and development of the chick.
- 3. The effect of the type of lighting on the growth and development of the chick.
- 4. The effect of the type of ventilation on the growth and development of the chick.
- 5. The effect of the type of feed, housing, lighting, and ventilation on the growth and development of the chick.

The present study was designed to provide information on the effects of the following factors on the growth and development of the chick: (1) the effect of the type of feed, (2) the effect of the type of housing, (3) the effect of the type of lighting, and (4) the effect of the type of ventilation.

5.0 RECOVERY OF DILUTE AQUEOUS BUTANOL BY ADSORPTION ON LIGNIN

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ABSTRACT

This concept addresses a novel technique for concentrating dilute aqueous butanol and acetone for recovery, using lignin derived from sulfuric acid hydrolysis of biomass. Billions of pounds of butanol are produced annually from petroleum for producing plastics, solvents, and coatings. Butanol specifically can be used in producing butyl acetate, butyl acrylate, and dibutyl phthalate. In addition, butanol is a solvent in the manufacture of oils, drugs and perfumes and in the production of urea-formaldehyde finishing compounds (Sherman 1978). The finishing compounds are widely used in the textile industry in manufacturing durable press finishing agents for cotton fabrics. Butanol also mixes well with gasoline, diesel, and vegetable oil fuels. It extends water miscibility tolerance of methanol mixed in gasoline and is less sensitive to phase separation in the presence of water when mixed alone with gasoline.

Butanol and acetone were derived through the acetone:butanol:ethanol (ABE) fermentation (with Clostridium spp. microorganisms) before 1930. After 1930, the fermentation route was gradually abandoned because of the development of chemical processes that synthesized butanol and acetone from less expensive petroleum. The current U.S. markets for butanol and acetone are 800 million and 1.6 billion pounds/year, respectively. The values of these products are \$0.30 and \$0.24 per pound, respectively (\$0.60 and \$0.53/kg) (Goldstein 1987). Because of their price and volume, butanol and acetone are considered commodities, and profitabilities are particularly sensitive to incremental changes in production costs. In producing alcohols from biomass, commercial viability depends on developing low-cost, energy efficient, recovery processes.

5.1 INTRODUCTION

Butanol fermentations are carried out under anaerobic conditions with Clostridium spp. Such fermentations are the major source of butanol and acetone in South America. Before 1930, butanol produced by fermentation was also the major source of the alcohol in the United States. As synthetic routes were developed for producing butanol from cheap petroleum, fermentation processes were abandoned. However, a recent analysis has suggested that if production costs of fermentation butanol can be reduced (Goldstein 1987), fermentation routes using Clostridium acetobutylicum may once again be potentially competitive with rhodium-catalyzed petroleum routes based on hydroformation of butanol from propylene.

Butanol is not only a product of the anaerobic C. acetobutylicum fermentation, but also the major toxic substance responsible for bringing a premature end to the fermentation at a concentrations of ca. 1.5% (Kuhn and Linden 1987). It appears that butanol tolerance can be enhanced by manipulating the cell membrane's fatty acid composition. Even so, the solvent concentrations that are possible (2% to 3%) would still be relatively low in the context of a commercial plant. Consequently, large improvements in recovery efficiency during fermentation are needed. Simultaneous benefits include 1) recovery of butanol, 2) higher fermentation productivity, and 3) reduced downstream separation costs.

5.2 ASSESSMENT OF THE CONCEPT

In the following sections, the proposed concept is described, and its technical feasibility, potential energy savings, current technologies, and potential markets are discussed.

5.2.1 Description of the Concept

Lignin is a relatively inexpensive material that occurs as a significant by-product from biomass processing. Its fuel value (based on Btu content) is about 2.5 to 4 cents/lb. If only 10% of the available cellulosic biomass is converted to oxygenated chemicals through bioconversion processes, an estimated additional 10 billion pounds/yr of by-product lignin could be produced (Sundstrom and Klei 1982). Lignin would be readily available in large quantities at the point of use, as a by-product of a biomass conversion process for producing butanol.

Preliminary research in our laboratory shows that lignin will adsorb butanol and acetone from dilute aqueous solution. Regeneration can result in a solution that is several-fold concentrated in butanol. This may prove significant in lowering the cost of subsequent distillation of the butanol. More importantly, the lignin adsorbs the alcohols but not the sugar from a liquid (aqueous) solution at ambient temperature. Thus, by combining adsorption with the fermentation to remove the inhibiting products, butanol, and acetone as they are formed, productivity could be significantly increased. Increasing fermentor productivity has been identified as a key problem to be solved to improve the economics of butanol production from biomass.

A typical acetone/butanol/ethanol (ABE) fermentation with *Clostridium acetobutylicum* yields butanol:acetone:ethanol at a molar ratio of ca 8:3.7:1 (Atkinson and Mavituna 1983). Because butanol and acetone are toxic to the microorganism, the fermentation is stopped at a product concentration of less than 2%. Products other than butanol are formed and include ethanol, isopropanol, and hydrogen. Lignin can selectively remove butanol, acetone, and ethanol (without removing sugar) at room conditions from liquid solutions.

5.2.2 Technical Feasibility

Lignin was packed into a column as a dry powder using standard procedures for chromatography columns. The lignin was obtained by acid hydrolysis of black locust trees, first in 5% H_2SO_4 , under reflux, for 4 to 5 hours. The material was then washed, and hydrolyzed again for 4 to 5 hours in 20% H_2SO_4 , under reflux. The remaining material was washed over a Buchner funnel until the wash water was at pH 5. The solids were then air dried. For purposes of this paper, this material will be referred to as "lignin," although this material most likely also contains residual cellulose. The effects of acid strength and other factors on hydrolysis are discussed in Bienkowski et al. (1984). Properties of lignin obtained by acid hydrolysis have recently been characterized by Glasser and Strickland (1987).

The dimensions column were 6 mm in diameter x 52.5 cm long, with a volume of 14.8 ml. The outlet and inlet of the column were capped with a 10-micron end fitting in order to retain the lignin. The weight of lignin packed was 10.88 grams (dry weight basis). Runs consisted of injecting 20 microliter samples of 1% to 2% solutions of the components shown in Table 5.1, and then eluting with water at a flow rate of 0.60 ml/min and a temperature of $30 \pm 0.05^\circ C$ in the type of apparatus shown in Figure 5.1. The results were used to characterize sorbent properties using standard calculations (see Ladisch, Voloch and Jacobson 1984; Neuman, Rudge and Ladisch 1987) and chromatography operating procedures (Ladisch and Tsao 1978).

The void fraction of volume external to the lignin particles was 0.40 (based on dextran). Most of the pores appear to be smaller than about 20 to 30 Å (based on polyethylene glycol (PEG) elution). The internal and external void fraction of the column is about 0.63 (based on NaCl). There is little or no adsorption of glucose (separates at about the same time as NaCl), and strong adsorption of butanol (separates at 27.2 ml volume), with an estimated capacity factor for butanol of 3.6 (which is quite large). Based on an analysis first presented by

TABLE 5.1. Elution Volume of Components Injected into a Column Packed with Lignin

Component	Molecular Weight	Elution Volume (ml)
Dextran	5 to 40 x 10 ⁶	5.9
PEG	20,000	7.4
NaCl	58.5	9.4
D-Glucose	180	9.9
MeOH	32	11.0
EtOH	46	11.8
Acetone	58	15.7
BuOH	74	27.2

Lapidus and Amundson (1956), the volume of feed, $\bar{V}$, which will saturate a column packed with adsorbent, is given by

$$\bar{V} = V_0 + KV_s \quad (1)$$

This assumes linear equilibrium. The parameter $\bar{V}$ represents the point of inflection on a breakthrough curve, and coincides with the peak maximum of chromatographic peak for a small sample size. On this basis, a first measure of column capacity can be estimated for the alcohols and acetone, based on $\bar{V}$, and assuming that the breakthrough profile is sharp. The result is as follows (data from Table 5.1):

$$\begin{aligned}
 x &= \frac{(\bar{V} - V_0)(0.01 \frac{\text{g butanol}}{\text{ml}})}{10.8 \text{ g lignin}} \\
 &= \frac{(27.2 - 5.9 \text{ ml})(0.01 \frac{\text{g butanol}}{\text{ml}})}{10.8 \text{ g lignin}} \\
 &= 0.02 \frac{\text{g butanol}}{\text{g lignin}}
 \end{aligned}$$

FIGURE 5.1. Apparatus for Evaluating Lignin Adsorption Properties

(i.e., the loading is 2%). On a similar basis the capacities for acetone, ethanol, and methanol were estimated to be:

- methanol - 0.5%
- ethanol - 0.56%
- acetone - 0.91%.

The apparent capacity is expected to increase significantly with decreasing temperature and increasing alcohol concentration. If the adsorbent proves stable under repeated use, its cost could be negligible. For example, the assuming lignin is used for 100 cycles, the sorbent cost per pound of butanol recovered would be about 1 cent.

Other preliminary research shows that adsorption and regeneration with hot CO₂ (a gas) yields an 8% alcohol product (which is 4 times as concentrated as in the beer). After regeneration, the lignin still retains adsorption capacity. Thus, the possibility exists that a relatively inexpensive adsorbent obtained as a by-product of biomass hydrolysis can be used in connection with an ABE fermentation to adsorb alcohols as they are formed and increase productivity by relieving inhibition. The research reported here evaluates improvements in the efficiency of the acetone/butanol/ethanol (ABE) fermentation based on the assumption that an adsorption process is combined with the fermentation. The effect of adsorption characteristics on improving energy efficiency and economic potential of the ABE fermentation is discussed in the following section.

5.2.3 Potential Energy Savings

The behavior of butanol and water is complex. At concentrations below 3 mol % (11.3 wgt %) and above 40 mol % (73.3 wgt %), the liquid composition is homogeneous (i.e., single phase). Between these concentrations two layers will form in the liquid phase. At equilibrium the compositions of these phases are 3 mol % butanol for the bottom layer and 40 mol % for the top layer. At 25 mol % (57.8 wgt %), a heterogeneous azeotrope forms and thus the vapor and average liquid compositions are equal. However, the liquid at 25 mol % will be separated into two layers with one layer at 3 mol % and the other at 40 mol %. Traditional distillation involves distilling off neutral solvents (butanol, acetone, and ethanol) with some water from the fermentation of beer. The overhead vapor is condensed. The resulting liquid separates in a decanter into two phases (since the butanol concentration is between 3 and 40 mol %). The lower phase is returned to the first distillation column while the upper phase is fed to subsequent columns for further purification. In the case of butanol and water alone, the remaining water with some butanol is boiled off in a second column. This vapor is condensed and returned to the decanter. Pure butanol product is obtained from the bottom of the second column.

While distillation appears to be somewhat inefficient because of the low starting concentration of neutral spirits in the fermentation beer, distillation is still reported to be more economical than crystallization or traditional extraction. However, even a small increase in fermentation beer strength would significantly reduce energy consumption. For example, increasing alcohol concentration from 2% to 4% decreases by half the amount of water which must be removed per pound of final product obtained.

An estimate of variable costs for the acetone-butanol fermentation from molasses is summarized in Table 5.2 (Hacking 1986). As the table shows, substrate costs dominate, while energy costs are the second major item. A 50% decrease in energy consumption would reduce variable costs by 5%. While this value seems small, it is a significant savings because the product cost would be reduced by 1 cent/lb solvent. Clearly, an economically viable method for improving separation efficiency must be inexpensive.

A much bigger relative impact would be evident in processes that use butanol as a solvent. In this case solvent recycle would seem necessary because of butanol's cost (30 cents/lb). Consequently, cost savings in the solvent recovery step would have an almost directly proportional affect on reducing the cost of using the solvent.

TABLE 5.2. Approximate Variable Costs per 1000 kg Solvent^(a)

Molasses, 5 te ^(b) at \$80/te	\$400
Ammonium Sulphate, 100 kg at \$80/te	8
Calcium Carbonate, 140 kg at \$50/te	7
Steam, 2.25 te at \$20/te	45
Total	\$460

(a) Refers to acetone + butanol + ethanol.

(b) Metric ton.

The overall manufacturing cost of butanol will be \$0.30 to \$0.40/pound in an economically viable process (Goldstein 1987). The estimated costs of current process technologies are two to three times higher, according to Goldstein, in part due to low fermentor, volumetric productivities. Adsorption of the alcohols by lignin may also increase productivity, by partially removing inhibition and thereby lowering fermentation costs.

5.2.4 Current Technologies

The practical and technical option for butanol recovery appears to be distillation, which was summarized in Section 5.2.2. Another option recently described in the literature involves using liquid membranes to concentrate butanol and acetone by pervaporation (Matsumura and Kataoka 1987). That process entails supporting oleyl alcohol on a hydrophobic membrane. In this system, concentration of butanol from 0.4% to 40% was reported, with the membrane having a separation factor (butanol/water) of 180 and an operational stability of at least 100 hours. The liquid membrane system is technically interesting, but at this time information on membrane cost is insufficient, particularly concerning potential oleyl alcohol losses and the cost of these losses.

5.2.5 Potential Markets

Markets for adsorption technology using lignin include fermentation processes that produce butanol and industrial processes that use butanol. Those markets include the following:

1. fermentation processes for butanol production (a long-term prospect because the United States currently has few, if any, commercial plants).
2. dehydration and recovery of butanol in order to recycle the alcohol in an alcohol pulping process
3. general solvent recovery of water discharge streams containing low levels of butanol.

Other uses will become apparent as research proceeds.

The emphasis of biomass research in recent years has been on the converting cellulosic residues to ethanol. However, the sugars obtained from biomass can be fermented to other key products, including acetone and butanol, which are "building blocks" for the chemical industry. Examples of key intermediates that can be derived from butanol and acetone include butyl acrylate, butyl acetate, and methyl methacrylate. Therefore, depending on the selectivity of a lignin adsorbent, this technology may find use in these other applications.

5.3 FUTURE CONCEPT DEVELOPMENT

Industrial-scale fermentation is currently carried out in South Africa using *C. acetobutylicum* in the Weizmann Process to produce ABE in a two-day fermentation. On a weight basis, this fermentation produces butanol:acetone:ethanol in a 6:3:1 ratio with CO₂ and H₂ as the other by-products. The yield of major products based on the sugar fermented is 30% solvents, 50% CO₂, and 2% H₂. The characteristics of the microorganism are

such that during the exponential growth phase, acid production predominates; whereas, during the stationary phase, solvent production is enhanced. The pH of the fermentation also affects the types of products formed. At high pH conditions, organic acid production is enhanced; at low pH solvent, production is favored. As the discussion above indicates, the fermentation must be carefully controlled to obtain the desired product. Inhibition of the fermentation is the major practical problem.

If the lignin is to be useful in a practical adsorption process, it must be capable of being regenerated. Desorption using 80% ethanol at 20°C gave good results. When excess liquid in the column was blown out with air and then a volume of 4.5 ml of 80% ethanol was passed through the column at 20°C, all of the butanol (as determined in experimental accuracy) was washed out. Surprisingly, the butanol desorbed initially was concentrated by a factor of almost two times. The desorption curve obtained was quite sharp. This run showed not only that the lignin could be regenerated but also that the butanol is separated in a more concentrated form. Further efforts are now needed to characterize desorption characteristics, and adsorbent stability. Studies with fermentation broths that contain cell debris and other media components also need to be conducted.

5.3.1 Steps Immediately Required

Our preliminary research has shown that lignin has the potential to selectively adsorb butanol, acetone, and perhaps ethanol from fermentation broth containing sugar and salts. After adsorption, the lignin can be regenerated by passing CO₂ gas at 90°C. The lignin was shown to retain its adsorption capacity after regeneration with CO₂. Further preliminary runs are now needed to define adsorption capacity and to specify an approximate range of desired operating conditions.

5.3.2 Additional Steps Needed for Implementation

Preliminary research confirms the hypothesis that lignin sorption of butanol can significantly reduce butanol production costs. Further developmental effort should be vigorously pursued. Specifically, engineering data for designing large-scale systems should be obtained, and a scaleup trial should be pursued. Other sources of lignin from the pulping industry should also be examined.

If scaleup trials are successful, the next step would be to seek a suitable company that either manufactures butanol or needs to recycle this solvent. At the same time, a company should also be identified that can build turnkey sorption systems and provide technical services to users of a lignin sorption system. Negotiations on technology transfer could then be initiated.

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WASTE/FUEL RECOVERY

6.0 POTENTIAL FOR BROADER APPLICATIONS OF EXTRACTING HYDROCARBONS USING LIQUID-CORE POLYAPHRONS

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ABSTRACT

A proposed concept is being developed to extract the bitumen from tar sands at low temperatures using liquid butane made up into a water-continuous polyaphron as the extractant. The sand breaks up the polyaphron so that the mixture separates into three layers: sand at the bottom, an intermediate aqueous layer, and a butane-bitumen solution on top, which can easily be separated from the other layers. From that solution, the butane can be boiled off and recovered to be reliquefied and reused. This should be a cheaper procedure than the hot water extraction method currently in use.

Evaluation of the proposed concept revealed the following:

1. Tar sands represent a significant energy reserve.
2. Hot water extraction as practiced in Alberta is energy intensive and unique in that many tar sands require different treatment.
3. Aphrons made of kerosene or butane can effectively remove bitumen from tar sands that are not suited to hot water treatment.
4. Liquid butane in polyaphron form as the extracting solvent has potential for simple cold separation and can be recycled.

6.1 INTRODUCTION

Many countries have vast reserves of hydrocarbons that are tied up in a highly viscous structure ranging from deformable oily sands to rock-like tar sands. These hydrocarbons are known as bitumen, tar, oil, or sometimes as heavy crude sands. They are characterized by an organic component that is valuable but virtually immobile because of its high viscosity. The structure of this component is made up of high-molecular-weight carbonaceous chemicals containing less hydrogen than occurs in crude oil. Embedded in this mass is a considerable quantity of inorganic mineral matter made up of sand, silt, and clay with a small amount of kerogen, a solid organic residue that is insoluble in most solvents.

Recovering the bitumen, as the sticky organic matter is sometimes called, poses a considerable engineering problem because its high viscosity makes it difficult to separate from the inorganic particles which, being finely divided, tend to adhere firmly to the bitumen. It is important to distinguish between these minerals and oil shales which contain virtually no oil, just kerogens. The proposed concept cannot be used for extraction from oil shales.

Tar sands are common in many regions containing oil deposits. The largest deposits are found in Venezuela, although they do not appear to have been commercialized. The North American continent has vast deposits in Alberta, Canada, where commercialization is occurring. Considerable, but little known, deposits are found in the central part of the United States, particularly in Utah, but these too have not yet been commercialized. Kentucky also has considerable deposits, but past attempts to develop them have failed and no further attempts appear to have been made.

6.2 EXISTING TECHNOLOGY FOR RECOVERING BITUMEN

The only commercially successful method for separating the bitumen from the sand is operating in Alberta, Canada. That method involves reducing the bitumen's viscosity by raising the temperature using steam, until the droplets of oil coalesce, and then separating the oil droplets from the inorganic material. However, this method only works on the type of deposits found in Alberta, where the inorganic mineral is sheathed in a very thin aqueous layer that separates the mineral from the oil. That type of deposit is unusual; in many deposits, the oil itself wets the minerals so that separation involves the step of replacing the oil adhering to the surface of the mineral with water.

A second problem with the existing method occurs after the separation stage and poses a possible environmental hazard. Because the clay particles are so small, they tend to remain suspended in the water and are very difficult to flocculate or settle. The wash water therefore cannot be discharged into rivers and requires very large dams for storing the effluent.

6.3 CONCEPT DESCRIPTION

The viscosity of bitumen can be reduced by using a solvent in the form of a polyaphron biliquid foam. If liquid butane is used as the solvent (instead of kerosene, for example) in the biliquid foam, the solvent can be recycled without consuming much energy.

In the following sections, the feasibility of using polyaphrons for extraction is discussed in general. That discussion is followed by a more detailed discussion of kerosene (used in earlier experiments) and then liquified butane as the solvent.

6.3.1 Polyaphrons

Biliquid foams exist, in which a nonpolar liquid, instead of gas bubbles, are found in the spaces between the continuous aqueous layers. The nonpolar liquid, like a gas bubble, is encapsulated in a thin soapy film. A polyaphron is a concentrated biliquid foam that can contain up to 96% of the nonaqueous phase dispersed in water in globules that have micron or submicron diameters (Sebba 1984). Such polyaphrons are stable enough to last for years, but will break under certain conditions. Because of those conditions, kerosene-based polyaphrons are opening up a novel extraction method that offers many advantages.

By juxtaposing minute kerosene globules to a detergent solution that can wet the solids and coat them, the oil can be prevented from re-adhering to the solids. This effectively is the same as the detergency process known as "rolling up." Although the encapsulating soap film surrounding the aphron is very tenacious, it is readily broken on contact with a hydrophobic material. In this way, the kerosene becomes available to dilute and mobilize the bitumen. However, the ingredients for making aphrons are still there, so the aphrons can be spontaneously reconstituted and reused (Sebba 1984, 1987).

The polyaphrons used in recovering bitumen must fulfill two requirements, so not all types of polyaphrons are equally suitable. The first requirement is that the surfactant in the aqueous phase must not have a tendency to adhere to the solid mineral with the hydrophobic end facing outward. That adhesion would make the solid nonwetable by water and would introduce a tendency for the oil to wet it. Because clays and silica are usually negatively charged, cationic surfactants cannot be used. Because their head groups are negatively charged and therefore repelled by the negatively charged solids, anionic surfactants could be used; in particular, sodium dodecylbenzene sulfonate has been found useful because it stabilizes good polyaphrons. The second requirement is that the oil used in the polyaphron must have a good solubility for the bitumen and be relatively cheap. Kerosene has shown itself able to fulfill these requirements.

6.3.2 Effectiveness of a Kerosene Polyaphron Extraction

Considerable, as yet unpublished, work has demonstrated the effectiveness of the extraction on many different samples of tar sands, both from the United States and Canada. When the extraction is performed batchwise in beakers, the residual sand has been found to be virtually free of oil.

A continuous process using a revolving tube, somewhat like a cement mixer, has been developed and tests to date have been most encouraging. However, one economic difficulty needs to be overcome: the amount of kerosene needed to liquefy the bitumen and the amount of bitumen that is recovered is about the same. Recovering the kerosene for reuse would require a distillation process that would add energy costs to the process. Nevertheless, the polyaphron extraction might prove to be preferable to present extraction methods because it is a cold process.

If the extract were to be used as a fuel oil and burnt, the kerosene may not need to be recovered. However, a possible alternative that would allow the solvent to be recycled without consuming much energy uses liquefied butane in polyaphron form as the extracting solvent.

6.3.3 Extraction by Liquid Butane

Butane has a boiling point of -0.3°C , and is a liquid at pressures above 2 atmospheres at room temperature. Experiments have shown that liquid butane, just like any hydrocarbon, can be converted into a polyaphron. It has also been shown that other hydrocarbons such as hexane, gasoline, and limonene can extract bitumen from tar sands. Experiments have confirmed that a butane polyaphron can behave in a similar way. The butane polyaphron has to be produced and extracted under pressurized conditions, if performed at room temperature, but the pressure required would be low enough not to present any problems.

The advantage of using butane as the solvent is that when the extract is decompressed to atmospheric pressure, the butane boils off and can be recompressed and reused. The energy savings should be significant. However, if the butane is kept below its boiling point of -0.3°C , it can be converted into a polyaphron at ambient pressure.

Procedure for Extraction by Butane

Butane, obtained from a cylinder, has been converted into a polyaphron by the following procedure:

1. One hundred ml of butane was transferred into a stoppered conical flask already containing 0.5 ml of tergitol 15-S-3, an oil soluble non-ionic surfactant, which was resting in a cold bath at -5°C .
2. Another similar flask cooled to the same temperature held 5 ml of water containing the surfactant dodecylbenzene sulfonate at a concentration of 5 g/liter.
3. The solution in this second flask was converted into a foam by shaking the flask. The butane was then added by shaking only a few drops at first, but increasing the amounts in an approximate geometric progression. This method fairly quickly incorporated all the butane into the water in the form of a biliquid foam. This produced a product in which the butane globules were no more than a few microns in diameter, encapsulated in a thin soapy film and dispersed in the aqueous phase in the form of a biliquid foam, or polyaphron. As long as this biliquid foam was kept below the boiling point of the butane, it remained stable.
4. Ten grams of tar sands obtained from Utah were broken into nuggets about the size of small nuts simply by hammer blows. (Mechanical crushing of tar sands into smaller fragments is not easy because of the plastic nature of the matrix.)
5. After they were precooled, these nuggets were shaken into the previously prepared polyaphron and shaken vigorously for a few minutes, taking care to keep the mixture cold.
6. The aphrons immediately attacked the tar sands, liquefying the bitumen because of the presence of the butane, and thus liberating the sand that became wetted by the water, which in turn displaces the bitumen. Adding a

further small amount of water allowed the bitumen to be completely separated from the sand. Because the bitumen is lighter than water, it floated above the surface of the water.

7. The mixture quickly separated into three clearly demarcated layers:

- the sand settled on the bottom, already remarkably clean
- water containing some dispersed clay and a small amount of colloidal oil globules formed the intermediate layer
- the major part of the oil floated on the surface of the water, where it could easily be removed.

If the temperature were raised to ambient temperature, the butane could be distilled from the bitumen, recondensed and converted into a polyaphron, and recycled.

Although the residual sand was very clean, some black particles were dispersed through it. At first these particles were thought to be residual tar sands and therefore the separation to be incomplete. It was later found that the actual quantity of oil in the particles was minute. In fact, these particles turned out to be water globules coated with a thin layer of sand mixed with oil, which proved to be an effective barrier to the coalescence of the water globules.

These structures have some resemblance to what have been called invert aphrons, that is water globules stabilized by a thin coating of minute aphrons. Grinding these particles with polyaphrons broke them up, but the quantity of oil recovered in this way most likely would not justify this further treatment. Because the number of particles remaining from the procedure seem to increase as the quantity of dilution water increases, only as much water as would enable the bitumen-butane solution to be floated should be used.

The efficiency of the extraction process was shown by another experiment. Thirty-five grams of tar sands from an unknown source in Colorado were shaken with 80 ml of a butane polyaphron of PVR 10. (PVR or phase volume ratio is the ratio by volume of oil phase to the water). The temperature was kept at -5°C . After the liquid was decanted off, another 80 ml of the polyaphron was added and the process repeated. The oil was removed by decantation after a small quantity of water was added. After the sand was dried and weighed, it was found that 69% of the oil had been extracted.

6.4 POTENTIAL ENERGY SAVINGS

If butane polyaphron extraction method can be made operational, considerable energy should be saved compared with the current state of the art. The method practiced in Alberta uses steam that has to heat up not only the bitumen but also the underlying sands. Because these comprise 90% of the tar sands, considerable amounts of heat are wasted. Butane extraction would work at ambient temperature if the operation were conducted under slight positive pressure and then boiled off simply by reducing the pressure. Some energy would be consumed in compressing the butane, but this physical process at such a small pressure requires considerably less energy than does steam generation or distillation.

A possible spinoff of this work, although not undertaken in this project, is that it could provide preliminary experience on pressurized polyaphrons, which would encourage future work on using butane polyaphrons, or possibly carbon dioxide polyaphrons, for tertiary oil recovery. Unfortunately, in the oil recovery industry many factors besides technological problems prevail, such as politics and economics.

The price of oil will eventually increase, which will allow alternative sources to be exploited and make tar sands a competitive source of oil. This novel extraction technology might make it competitive now. Most important, however, is that oil is a limited but vital resource in any country, and tar sands provide an alternative source that is available in large quantities in some countries, including the United States. Therefore, this country should be in a position to develop this alternative resource at very short notice, if the need arises.

6.5 FUTURE DEVELOPMENT NEEDS

Further experience with this extraction method is expected to significantly improve its efficiency. This method, like the hot water extraction, has the disadvantage that the water layer still contains some finely dispersed oil and clay. This can be removed by a combination of colloidal gas aphron flotation and flocculation by aluminum ions, such as has been effectively used for cleaning the waste waters in Florida phosphate operations.

It must be stressed that, when working in the area of surfaces, extrapolation may be misleading. For example, it would be thought that if the aphrons were made smaller the extraction would become more efficient. Experiments have disproved that idea because the encapsulating soap film has to be broken to release the solvent that is to liquefy the bitumen. This film is broken because fine spikes of hydrophobic tar sand, when they touch the outer surface of the soap film, create a high contact angle and penetrate the soap film, breaking it. If, however, the aphron is small compared with the irregularities on the tar sand, geometric considerations will prevent this penetration, and the process will not work. For that reason, the procedures suggested in this proposal must be tested experimentally.

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It is well known that the rate of reaction is affected by temperature. In this experiment, the rate of reaction was measured by the volume of gas evolved. The reaction was carried out at three different temperatures: 20°C, 30°C and 40°C. The results are shown in the table below. It can be seen that the rate of reaction increases as the temperature increases. This is because the molecules have more energy at higher temperatures and are therefore more likely to collide with sufficient energy to overcome the activation energy barrier. The rate of reaction is also affected by the concentration of the reactants. In this experiment, the concentration of the reactants was kept constant, so the effect of temperature was the only variable. The results show that the rate of reaction is directly proportional to the temperature. This is because the rate of reaction is determined by the number of successful collisions per unit time, and the number of successful collisions increases as the temperature increases.

2. CONCLUSION

The results of this experiment show that the rate of reaction increases as the temperature increases. This is because the molecules have more energy at higher temperatures and are therefore more likely to collide with sufficient energy to overcome the activation energy barrier. The rate of reaction is also affected by the concentration of the reactants. In this experiment, the concentration of the reactants was kept constant, so the effect of temperature was the only variable. The results show that the rate of reaction is directly proportional to the temperature. This is because the rate of reaction is determined by the number of successful collisions per unit time, and the number of successful collisions increases as the temperature increases.

7.0 FUEL FROM MUNICIPAL SLUDGE

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ABSTRACT

A proposed process is being assessed for separating a significant fraction of organic material from municipal sludge by acid extraction and for reconstituting the extracted organic material as a solid fuel. Organic compounds that have unshared electron pairs or unsaturation in the form of double bonds or conjugated double bonds protonate and dissolve in concentrated protonating acids, such as sulfuric acid. These dissolved organic compounds can be recovered unchanged, by precipitation, when diluted with water.

Experimental results demonstrated that 80% of the solids can be dissolved during acid extraction, and up to 25% of the initial solids can be precipitated when diluted with water. The precipitated product was a high organic (90% to 98%) solid and represented up to 30% of the initial organics. Preliminary economic estimates show this process to be competitive with other sludge disposal and reuse alternatives for wastewater treatment plants serving one million people or more. The economic picture can be greatly improved by incorporating the negative cost of sludge disposal.

The assessment results suggest that future work is needed to optimize the protonation process and operating conditions, to select and design an acid recovery system, and to recover and reuse the inorganic residue. The proposed activities would provide a basis for a detailed economic analysis and pilot plant design.

7.1. CONCEPT ASSESSMENT

In the following sections, the results of the preliminary concept assessment are presented. First, the proposed concept is described. Then, the results of the analyses of its technical feasibility and economics are discussed. Finally, current and competing technologies and potential markets for the concept are described.

7.1.1 Description of the Concept

Thermal energy recovery from wastewater sludge by direct combustion is theoretically achievable for moisture contents as high as 20%. However, because of the high ash content of the sludge (20% to 30%), its fuel value is very low. The purpose of the proposed concept is to separate a significant fraction of the organic material from the sludge by extraction and to reconstitute the extracted organic material as a solid fuel.

When sludge (a mixture of organic and inorganic compounds) is contacted with an acid (in this case, sulfuric acid), the acid may behave as a solvent or reactant, or may have no impact on the organic material. The most desirable option for producing a high-grade solid fuel is to solubilize the organic fraction of the sludge. Solubilization allows the organic fraction of the sludge to be dissolved and reconstituted as a solid in a dilute (sulfuric) acid solution. Concentrated sulfuric acid, in behaving as a solvent, resembles water in that it self-protonates to produce acidic (H_3SO_4^+) cations and basic (HSO_4^-) anions. When an organic compound is placed in a highly protonating solvent (such as sulfuric acid), the hydrogen ion from one molecule of sulfuric acid will often preferentially protonate the organic molecule rather than another molecule of sulfuric acid, as shown in Equation 1.

Organic compounds that have unshared electron pairs available for bonding and compounds that have unsaturation in the form of double bonds or conjugated double bonds protonate and dissolve in concentrated sulfuric acid (Liler 1971), as shown in Equation 1.

To use the dissolution character of organic materials in concentrated sulfuric acid, it is necessary to protonate (dissolve) the organic compounds, separate the dissolved from the undissolved materials, deprotonate (precipitate) the dissolved organics, and separate the precipitate from the deprotonating liquid. The proposed process flowsheet, shown in Figure 7.1, includes facilities for sludge and acid storage, protonation and deprotonation reactors, a settling tank, two centrifuges, a dryer, and storage facilities for final product and undissolved residue. All proposed processes use standard unit operations equipment that has protection against acid corrosivity. No details of the acid recovery system are included at this time.

7.1.2 Technical Feasibility

The technical feasibility of the proposed process concentrated on three major areas:

- identifying effective acid solvents
- establishing reasonable operating conditions
- determining the product's recovery and composition.

Each areas is discussed below, followed by a discussion of two process impediments that were identified.

FIGURE 7.1. Flowsheet for a Proposed Sludge-to-Solid Fuel Processing Plant

Identifying Effective Acid Solvents

An extensive literature search was conducted to identify acid solvents that would selectively extract the organic fraction from municipal sludge. The search identified several articles (Gillespie and Leisten 1954; Gillespie and Robenson 1959) and a comprehensive treatise on reaction mechanisms of organic compounds in strong acid media (Liler 1971). This literature supported protonation as the controlling factor in the effectiveness of acids to selectively dissolve (extract) the organics from a matrix of organic and inorganic compounds. The literature also indicated that acids with high protonating ability are the most effective in dissolving organic base.

Much of the reported work has centered on the specific study of acid-catalyzed reactions. In those studies sulfuric acid/water mixtures were used because of their high degree of self-protonation. Other acid solvents that have a self-protonating ability similar to that of sulfuric acid are the mixtures of hydrogen fluoride/boron trifluoride and fluorosulfuric acid/antimony pentafluoride. Strong acids such as nitric acid and hydrobromic acid, and superacids such as perchloric acid would also be expected to have protonating abilities similar to those of sulfuric acid (Liler 1971). Sulfuric acid was selected as the solvent for this study because it has a high autoprotolysis constant.

Establishing Reasonable Operating Conditions

A series of bench-scale batch experiments were conducted with sulfuric acid to establish 1) reaction time and optimum acid strength and 2) reactant ratios. The results of the experimental program, discussed below, were used to establish practical (preliminary) processing conditions for an economic analysis of the industrial-scale sludge-to-solid fuel process shown in Figure 7.1.

The time required for the maximum extraction of the soluble fraction of the dry sludge and the ultimate product yield and quality vary with acid strength, temperature, and the degree of agitation (mixing). The criteria for the optimum strength of the acid are determined based on considerations of acid effectiveness for dissolving and reconstituting organics. Because acid strengths of less than 20 Normality (N) were ineffective, acid strengths of only 36, 27.5 and 20 N are reported in this study. Figure 7.2 shows the dissolution of total solids for the three acid strengths as a function of time at room temperature. For all experiments the acid-to-dry sludge ratio was held constant at 20 ml/g.

The data suggest that maximum dissolution of sludge is accomplished at about 24 hours for 27.5 and 36 N acid strengths. Although the dissolution increases with time for 20 N acid strength, other experiments show that the final product recovery is poor.

To examine the effect of varying the reactant ratio on the percentage of dry sludge dissolved, various volumes of 27.5 N H_2SO_4 were used for a fixed weight of dry sludge (3 g). Three local maxima in "the percentage of sludge dissolved as a function of reactant ratios" were observed. The maxima occurred near ratios of 20, 40, and 85 ml of 27.5 N H_2SO_4 /g of dry sludge. This pattern is similar to that observed by Senftle et al.^(a) and is expected to vary with changes in temperature and acid strength.

Determining Product Recovery and Composition

The amount of solid fuel product and the percentage of organics in the product recovered from the sulfuric acid solution were studied as a function of reaction time for different strengths of the dissolving acid solvent and are shown in Table 7.1. The maximum recovery of the solid product ranges from about 20% to 25% using 36 N H_2SO_4 . This recovery is a function of the dilution factor and the temperature.^(a) In a similar study with H_2SO_4 , product recovery as high as 35% was obtained, with over 99% of the product being organic material.^(a) In this study the

(a) Senftle, F., et al. 1988. "Low-Ash Solid Fuel Via Acid Extraction from Sewage Sludge." U.S. Geological Survey, Confidential Report.

FIGURE 7.2. Dissolution of Total Solids for the Three Acid Strengths as a Function of Time at Room Temperature

final product is also rich in organics (greater than 98% in all cases). Results of C, O, H, and N analyses reported by Hackney^(a) in a preliminary study indicate that heating values of the final product (obtained from a similar process) vary from 31×10^6 J/kg to 34×10^6 J/kg.

Process Impediments

Although the process for extracting organic material from the municipal sludge has been technically demonstrated, two process impediments have been identified based on the results to date.

The first impediment is the relatively low yield of the process. As indicated by the experimental results, reconstitution of less than 25% of the original product was achieved after deprotonation. Although the reconstituted material was very low in ash content, it represented only 20% to 30% of the theoretically recoverable organics. The recovery appears to be limited by the thermodynamics of the process. The composition of the sludge needs to be analyzed to determine if the undissolved materials are of the saturated hydrocarbon type, in which case, a multistage acid extraction system might be applicable, or whether adjustment of experimental conditions (e.g., temperature, type of solvent) might enhance the dissolution and reconstitution of the organic fraction.

The second impediment is the need to develop an acid recovery system and a way to recover and recycle any other additives used in the protonation or deprotonation steps. Concentrated sulfuric acid has been extensively used as a catalyst and as a reaction medium for fertilizer production, pigment and paint preparation, etc. Acid

(a) Hackney, P. 1988. "Low-Ash, Low-Sulfur Fuel Via Sulfuric Acid Extraction of the Organic Matter in Sewage Sludge." ME Thesis, Howard University, Washington, D.C.

TABLE 7.1. Solid Fuel Product After Deprotonation^(a)

Dissolving Acid Strength, Normality	Protonation Reaction Time, Hours	% Solids ^(b) Recovered	% Organics ^(b) Recovered	% Organics In Recovered Solids
27.5	1	5.42	8.92	95.9
	24	11.00	14.33	97.8
	36	12.88	18.58	98.4
	48	14.94	19.43	97.5
36	1	7.99	10.43	97.8
	24	18.59	24.29	98.0
	36	18.81	24.43	97.4
	48	22.79	29.71	97.8
20	1	3.43	4.18	91.4
	24	9.40	11.97	95.5
	48	10.44	12.66	90.93

(a) Reactant Ratio = 20 ml acid/gm of dry sludge. Deprotonation Dilution Factor = 900 ml H₂O/60 ml acid solution.

(b) Initial weight of dry sludge = 3.0 grams.

(c) Initial weight of organics in dry sludge = 2.25 grams.

recovery systems for these processes have been identified (Goers 1969; Umstead 1973; Peterson 1975). Therefore, applying the existing technology may help remove this impediment.

7.1.3 Economic Analysis

One of the most important criteria for determining the viability of a new technology is its ability to be economically competitive. To determine the concept's viability, the results of the concept's experimental program were combined with reported literature results and engineering judgment to formulate a preliminary cost estimate for comparison with other technologies.

Three significant deviations from the experimental program results were assumed for the cost analysis:

1. The ratio of acid to dry sludge solid was established as 10 ml of acid per gram of dry solid. This ratio was selected because operation at the experimentally determined local maxima provides only marginal increase in sludge dissolved at disproportionately higher costs. (A sensitivity analysis indicated that the overall costs were most sensitive to acid costs.)
2. The final acid normality was based upon the acid to dry solid ratio mentioned above, rather than the optimum acid strength as suggested from the experimental results.
3. An efficient industrial, multistage mixer was assumed to be able to achieve the same results during the protonation reaction in 30 minutes as the laboratory-scale mixer achieved in 24 hours.

Other assumptions made to facilitate the cost estimate are listed below (Peters and Timmerhaus 1980; Vernick and Walker 1980; U.S. Environmental Protection Agency (EPA) 1985):

- sludge production rate - 0.26 lb/capita/day
- feed sludge character - anaerobically digested at 20% solids
- protonation reactor - 35% of solids dissolved and density of reactants same as H_2SO_4
- deprotonation reactor - 95% of dissolved solids precipitated
- settling tank - negligible suspended solids in overflow and 4% suspended solids in underflow
- centrifuge(s) - negligible suspended solids in supernatant and 14% suspended solids in flake
- acid recovery and protection systems - 35% of capital and 20% of the operating and maintenance cost of plant
- acid and residue disposal costs - equal to value of metals/minerals recovered from residue
- plant life - 20 years
- interest rate - 10%
- process water - no cost
- depreciation - not considered.

Table 7.2 presents the production costs on a dry-metric-ton basis as a function of population and efficiency of the acid recovery system. The efficiency of the acid recovery system impacts the costs very dramatically. A 5% drop in the efficiency of the system can increase costs by 15% (100,000 population) to 64% (5 million population). For a 95% acid recovery and for populations greater than 1 million, the estimated cost is comparable to reported costs (EPA 1984) for land application (\$105), incineration (\$144), and composting (\$161)^(a) on a dry-metric-ton basis.

The costs presented in Table 7.2 do not include the negative cost of sludge, i.e. the amount municipalities are paying for sludge disposal. Including this cost, which varies with the technique and the quantity of sludge disposed, would provide an even more positive comparison of this process to the conventional disposal techniques mentioned above. Unlike the competing technologies, discussed in the next section, the end product of the proposed process is a solid fuel, and the process has the potential to recover other materials from the sludge.

7.1.4 Current State of the Art and Competing Technologies

The following sections discuss the methods currently being used to reuse or dispose of wastewater sludge and competing technologies being investigated.

Current State of the Art

Currently, five methods are widely used to reuse or dispose of wastewater sludge: land application, land filling, distribution and marketing, incineration, and ocean disposal (EPA 1984). The selection and implementation of a particular disposal technique depend on many factors, including the source and quantity of wastewater sludge, geographic location of the community, hydrogeology of the region, land use, economics, public acceptance, and regulatory framework (EPA 1984). More often, a given municipality may have to use more than one technique to dispose of its sludge. Each disposal method is briefly described below.

Land application is defined as the spreading of sludge on or just below the surface of the land, whereas, land filling is the burying of sludge beneath a soil cover in a specially designated area. Currently, about 25% of the municipal wastewater sludge produced in the United States is disposed of by land application. A major impediment to future expansion of this option in urban areas will be the availability of land at a reasonable cost.

Distribution and marketing of sludge products are fast growing as an option for managing sludge. This option is based on the soil conditioning and fertilizing values of sludge, and is primarily carried out by medium- and

(a) Based on private communication in February 1988 with Mr. Francis Riddle, Water and Sewer Utility Administration, Department of Public Works, Washington, D.C.

TABLE 7.2. Production Costs (\$/dry metric ton) for a Sludge-To-Solid Fuel Processing Plant As a Function of Population Size and Percentage of Acid Recovery^(a)

Population Served	% Acid Recovery				
	95	90	85	80	75
100,000	470 ^(b)	541	611	682	753
200,000	373	444	515	586	657
300,000	324	399	470	541	611
400,000	300	370	442	513	583
500,000	280 ^(b)	280	350	421	492
600,000	198	269	339	410	481
700,000	191	262	333	404	475
800,000	185	255	326	397	467
900,000	180	251	322	393	463
1,000,000	151 ^(b)	221	292	363	434
2,000,000	131	202	273	344	415
3,000,000	122	193	264	335	406
4,000,000	117	187	258	329	400
5,000,000	112	184	254	325	370

(a) Does not include the costs of sludge treatment prior to final use or disposal; the costs are per dry metric ton of raw material processed in December 1987 dollars.

(b) These values were calculated. All other capital costs were obtained by scaling the calculated values according to the following:

Capital and O&M Costs (excluding acid) of b =
 (costs for a) X (population of b / population of a)^{0.6}. Acid costs were calculated in all cases.

and large-size municipalities. The cost of that option, however, may be relatively high compared with that of direct land application (EPA 1984).

Incineration is the burning of volatile materials in sludge solids in the presence of oxygen. This technique offers significant advantages compared with the other sludge disposal techniques because it reduces the sludge to a compact residue ash consisting of about 20% of the original volume of the sludge solid. Incineration also eliminates some potential environmental problems by completely destroying pathogens and reducing many organic chemicals. However, it is a very costly technique that is only affordable for large municipalities.

Ocean disposal, although still practiced by about 4% of the municipalities in the United States, is presently considered an unacceptable disposal option because of long-term environmental impacts.

Competing Technologies

Using sewage sludge to produce fuel oil and synthetic asphalt by direct thermochemical reactions is currently being investigated and has met with some success. Bayer and Kutubuddin (1982) have recently developed a technique to obtain oil from sewage sludge by heating the dry sludge to 300°C to 350°C in an oxygen-free environment for about 30 minutes. The oil product has a heat content of 37 to 42 MJ/kg (the heat content of coal ranges from 21 to 34 MJ/kg).

Bridle and Campbell (1983) have repeated Bayer's and Kutubuddin's procedure using Canadian sludges and confirm the formation of a straight chain hydrocarbon oil having a high heating value and a relatively low ash content.

On a dry-weight basis, sewage sludge contains 30% ash. By converting the sludge to an oil, Bayer and Kutubuddin (1982) have been able to separate the ash, which remains in the residual sludge, from the oil to produce a low-ash fuel oil with a high heating value.

Molton and Fassbender (1986) and Molton, Fassbender and Brown (1988) have demonstrated the feasibility of a continuous unit for converting primary sewage sludge to a burnable oil product. In a sludge-to-oil-reactor system (STORS), they report a 73% energy recovery in burnable products. An economic analysis was conducted for cities with populations of 10,000, 100,000 and 1 million, and the disposal costs per ton of sludge were calculated to be \$601, \$114 and \$45 (1983 dollars), respectively. These estimates were reported to be conservative and indicate that STORS has the potential for competing with incineration.

7.1.5 Potential Markets for the Concept

Sludge-to-solid fuel conversion, as an alternative sludge disposal technique, generates a high-grade, low-ash-content fuel and a residue containing a variety of useful metals. Because of this, any significant market analysis of this technology should address the following issues:

- sludge-to-solid fuel conversion as an alternative source of renewable energy
- fuel from municipal sludge as an alternative technique for sludge disposal
- inorganic residue from sludge-to-solid fuel conversion as source of valuable metals.

In Section 7.1.3, it was established that production costs of the sludge-to-solid-fuel process were lower than those of sludge incineration for large municipalities, if 95% of the spent acid could be recovered and recycled. A survey of 1011 treatment plants that generate 36% of the U.S. municipal wastewater sludge has shown that 32% of large treatment plants (greater than 10 MGD) use incineration before sludge disposal (EPA 1984). This suggests that a large market exists for new and cheaper sludge disposal techniques.

Although plants that convert sludge to solid fuel are not competitive as sources of cheap energy, the high-grade fuel they produce could be marketed without major difficulty. Also, the concentrations and types of metals in inorganic residue from such plants would depend primarily on the type and amount of industrial waste that is discharged into the municipal wastewater treatment system. The sludge inorganic residue could contain a diversity of metals (cadmium, chromium, copper, tin, zinc, titanium, silver, gold), which may have economic potential.

7.2 FUTURE CONCEPT DEVELOPMENT

This preliminary evaluation (Phase I) has determined the technical feasibility and the limits of the protonation and deprotonation steps of the proposed process. The assessment showed that the process can be economically feasible under certain conditions. The objectives of Phase II are to remove design uncertainties, to verify assumptions made for the preliminary economic assessment, and to optimize product recovery. The results of Phase II will form the basis for a pilot scale (demonstration) unit (Phase III). This demonstration unit will be operated on a continuous or semi-continuous basis to verify technically and economically the concept and design developed in Phase II.

The specific tasks to be conducted under Phase II are briefly described below.

Product Yield Improvement - The product yield was quite low in our experiments, with less than 25% of the original dry sludge being reconstituted after deprotonation. Although the reconstituted material was very low in ash content, it represented only 20% to 30% of the total recoverable organics. Determining the organic components in sludge will provide information about the types of acids and the design of the protonation reactor needed to improve the product yield. High protonating acid mixtures, acid/additive mixtures, and superacids will be investigated.

Selection of an Acid Recovery System - The work performed in this Phase I study identified several acid recovery systems that appear to have applicability in the excess acid extraction process (Goers 1969; Umstead 1973; Peterson 1975). A paper study of the candidate acid recovery system will be conducted to include preliminary cost estimates,

accessibility to technology (i.e., patent-right protection), and generation of additional waste streams. The most promising acid recovery system will be tested experimentally to collect thermodynamic and kinetic data required for commercial scaleup and detailed cost estimates.

Residue Treatment/Resource Recovery - The present work has indicated that approximately 40% of the solids in wastewater sludge will not dissolve under excess acid conditions in a commercially feasible time. This material, however, contains valuable minerals/metals in concentrations that may permit their economic recovery. This task will determine the technical feasibility of recovering these materials and the economics of using the residue (with and without mineral recovery) as a road/construction material, soil amendment, etc. The results of this task will impact the overall detailed economic assessment.

Optimization of Operating Conditions - Temperature, acid normality, and mixing patterns may be the major parameters affecting the protonation/ dissolution process. Some attempt was made to optimize the normality for sulfuric acid in this study. Further experiments will be conducted using the "best candidate" acid/additive for product yield to determine optimum operating conditions. This information will provide a basis for a detailed process mass and energy balance. This data will later be used for a scaleup design of pilot and commercial units and for the overall economic analysis.

Detailed Economic Analysis - The economic assessment conducted in Phase I was based on generalized cost fact sheets. A detailed cost estimate based on properly sized reactors, pumps, pipes, etc., and actual costs of operation, maintenance, and supplies will be calculated in this task. Total costs will be computed for multiple population levels on a basis of dry ton of sludge processed. This will facilitate a more accurate comparison of process costs to current reuse and disposal alternatives for sludge, such as composting, land disposal, and incineration.

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PROCESS EQUIPMENT

8.0 DEVELOPMENT OF AN ELECTROSTATIC AGGLOMERATOR

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ABSTRACT

The objective of this work was to analytically investigate an electrostatic agglomerator that is designed to control the fine particles in industrial processes and power plant flue gases. The operating principles of the agglomerator are simple. A flow of particle-laden gas is split into many branches. The branches are volumetrically equal, containing about the same number of particles with about the same size distribution. The particles are charged positively in the half of the branches and negatively in the rest. Subsequently, the streams are recombined in a manner that brings the oppositely charged particles into proximity. The small distances between the negatively and positively charged particles result in significant Coulomb forces. Particles with the same charge polarity repel each other, while those with the opposite polarity attract each other, which leads to interparticle contact and agglomeration. The agglomerated particles are subsequently removed from the gas stream by any conventional technique such as cyclones, filters, or an electrostatic precipitator (ESP).

Analyses have shown that the concept is feasible: particles can be charged and agglomerated, and the interparticle adhesion forces are strong enough to overcome collisional forces acting to break the agglomerates. The agglomerator can reduce both the energy consumption and the capital equipment costs of existing gas cleaning devices, and can reduce the costs of recycling particulate dust. The agglomerator can also reduce a respiratory health problem by increasing the efficiency of collecting submicron particles in existing filtration devices.

Funding is now needed to further develop the agglomerator concept. A two-phase program is recommended: Phase I would address near-term development and Phase II would address long-term development. In Phase I, a bench scale test should be conducted to verify and refine the theoretical model. In Phase II, a full-scale or pilot demonstration should be conducted to obtain durability and maintenance information, to optimize the operational aspects of the equipment, and to demonstrate the technology to industry. Throughout Phases I and II, a marketing effort is needed to identify the initial market niche for the agglomerator and to map out the most expedient path to commercialization.

8.1 INTRODUCTION

The emission of fine respirable particles or aerosols from coal-burning power plants represents a significant health and environmental risk. Fine respirable particles range in size from submicron to 10 microns in diameter. Particles 1 micron or smaller are considered the most dangerous (Meyer and Edwards 1978). Their toxic effect is the result of one or more of three mechanisms: 1) the particles are intrinsically toxic because of their chemical makeup; 2) the particles can adsorb toxic substances on their surface; and 3) the particles interfere with the mechanisms that normally clear the respiratory passages.

In addition to causing health risks, fine particulate emissions modify weather patterns because of their ability to absorb and scatter sunlight and to serve as condensation or freezing nuclei. Therefore, a strong incentive exists to control and limit as much as possible the particulate emissions from any source in general and from pulverized coal-burning power plants in particular.

Pulverized coal is burned in flight, suspended in the hot oxidizing atmosphere of a large boiler. The pulverization, the mode of combustion, and the nature of the coal all help determine the ash particle-size

distribution. Figure 8.1 shows the particle-size distributions of particles emitted from uncontrolled power plants. As the figure shows, as much as 50% of the mass of all emitted particles can be below 10 microns in diameter.

One possible approach for controlling and limiting particulate emissions is to remove the ash from the coal before it is burned. Although coal beneficiation will reduce the coal's ash content, it is likely to result in the emittance of smaller particles. Finer particles are produced because very fine coal pulverization is required to liberate and remove the small mineral and pyrite inclusions in the coal. In the process of fine pulverization, the large mineral inclusions are pulverized as well. Because the efficiency of most coal-cleaning processes decreases with decreasing particle size, coal beneficiation efforts can be expected to increase the fraction of

FIGURE 8.1. Size Distributions of Particles Emitted from Uncontrolled Power Plants (pulverized coal-fired boilers) (Shannon 1971)

micron-size particles in the boiler effluent. Therefore, flue-gas cleaning must be used to successfully reduce the particulate emissions when coal-cleaning processes are used before combustion.

However, existing flue gas cleaning techniques and devices exhibit decreasing removal efficiency with decreasing particle size, as shown in Figure 8.2. In the figure, the efficiencies of all the conventional gas-cleaning devices are plotted against particle size (Meyer and Edwards 1978). The figure shows that for a particle diameter of 1 micron or less, no device has a collection efficiency reaching 99% and that most conventional devices do not reach 99% efficiency even for particles with diameters of 5 microns. Therefore, to substantially reduce the emissions of micron or submicron particles, the existing techniques need to be significantly improved or new approaches need to be developed.

8.2 CONCEPT ASSESSMENT

In the following sections, the electrostatic agglomerator concept is described, and its benefits and technical feasibility are discussed. Also, impediments to wide-scale use of the concept, state of the art of competing technologies, and its market potential are addressed.

FIGURE 8.2. Extrapolated Collection Efficiencies as a Function of Particle Size for Various Filtration Devices (Meyer and Edwards 1978)

8.2.1 Description of the Electrostatic Agglomerator

To significantly improve the efficiency of particulate collection, several approaches could be considered. Purely inertial separation techniques would be inappropriate for particulate sizes ranging from 0.5 to 10 microns. The following devices could be considered:

1. improved ESPs
2. natural or synthetic fabric filters
3. agglomeration of small particles, followed by inertial or other conventional separation devices
4. innovative techniques that combine the features of the two or more devices listed above or that significantly improve them.

The proposed approach for the electrostatic agglomerator concept belongs in the third and fourth category. The operating principles are simple. A stream of particle-laden gas is split into many approximately equal streams, each containing roughly the same number of particles with the same particle size distribution. The particles are defined as solid or liquid droplets; they can be electrically conducted or insulating. The particles in half of the streams will be by some means charged positively and the other streams negatively charged. Then the streams will be recombined bringing the groups of oppositely charged particles into proximity, resulting in a significant mutually attractive Coulomb force. This force will cause the particles to agglomerate and remain active until each agglomerate reaches electrical neutrality. The agglomerates can be removed from the gas stream using any of the conventional existing approaches, such as cyclones, filters or ESPs.

Several geometries of flow dividers and particle chargers appear suitable for electrostatic particle agglomeration. The concept chosen is shown Figure 8.3. The incoming flow is split into many small electrically conductive channels that are square in cross-section. At the center of each channel is a high voltage corona wire. Each wire has a polarity opposite to its neighbor (except those on a diagonal). In this manner the particles emerging from a channel with a positive wire, hence charged positively, are completely surrounded by negatively charged particles emerging from the four surrounding channels. This is true for all channels in the matrix.

Each negative channel is surrounded on four sides by positive channels and vice versa. This facilitates rapid particle agglomeration because of three effects: 1) the fluid mechanical mixing of the streams, 2) interparticle Coulomb attraction/repulsion, and 3) the Coulomb force from the applied electric field between the high voltage wires. As in a conventional ESP, the particles migrate toward the collecting electrode (in our case the walls of the channels). Therefore, when the particles emerge from their respective channels, high particle concentration will occur along the perimeter of each channel relative to its center. Because all particles within the same channel have the same polarity, they will mutually repel each other, forcing them into a stream of oppositely charged particles emerging from the neighboring channels. Thus, both repulsive and attractive interparticle Coulomb force as well as the applied electric field force act in concert to create rapidly forming agglomerates.

The components of an agglomerator are shown in Figure 8.4. The agglomerator consists of an inlet plenum, a charger section that contains the channels, and an agglomeration section. Subsequently, agglomerates will be removed by a drop-out section or a cyclone separator. The particles are charged in the charging section and migrate to the channel walls. When they emerge from the adjacent channels, the oppositely charged particles combine because of the mutually attractive Coulomb force. Finally, the agglomerated particles are inertially removed from the gas stream.

A typical application for an agglomerator could be a 250-ton-per-day container glass furnace with particle laden gases flowing at 40,000 acfm. The agglomerator for this application would weigh about 12 tons and would be 7 ft x 7 ft x 2 ft.

FIGURE 8.3. The Proposed Electrostatic Particle Agglomerator Concept

8.2.2 Benefits

The agglomerator will combine fine particles into larger ones. In a gas stream with a single particle size uniformly distributed, the agglomerate size will be twice that of the entering particle. The agglomerate size will be larger because half the particles will be positively charged in the agglomerator and half negatively, and because each particle is likely to combine with another to become electrically neutral.

FIGURE 8.4. Schematic of an Experimental Electrostatic Agglomerator Indicating Traversing Optical Diagnostics (laser particle sizer)

For a broad particle size distribution similar to that shown in Figure 8.1, the particle size change can be much more dramatic than the example described above. For example, in a gas stream with particles of two different sizes, a large particle can become electrically neutral by capturing number of smaller particles (N)

$$N = \frac{r_L^2}{r_s^2}$$

where r = radius

L = large particle

s = small particle

because the charge on a particle is proportional to its radius squared. A particle with a diameter of 10 microns could capture and thus eliminate 10,000 particles of 0.1 micron diameter before becoming electrically neutral.

For clarity, the above example was given for only two particle sizes. However, the effect is qualitatively the same for realistic gas streams that have a large number of particle sizes. The resulting shift in the particle size distribution may allow the following benefits:

- reduced energy use and capital costs in flue gas clean-up equipment
- reduced costs of recycling
- decreased health hazard from fine respirable particles.

Each of these benefits is discussed below.

Reduced Energy Use and Capital Equipment Costs

As Figure 8.2 shows, ESPs or fabric filters must be used for particles below 5 microns. For a typical glass furnace, the installed costs of these devices range from \$1 million and \$1.5 million and the operating costs from \$150,000/year to \$250,000/year.

The agglomerator's installed cost would be about \$200,000, with operating and maintenance expenses at \$15,000/year. A 200-MW coal-fired power plant would require 8 such agglomerators, for an installed cost of about \$1.5 million. Operating and maintenance expenses would be about \$100,000/year. The agglomerator is expected to increase the particle size distribution to values larger than 5 microns, which would allow cyclones to be used. This would save about \$1 million on installed cost and most of the \$150,000 to \$250,000 on operating costs. The cost of the agglomerator would be low compared with the ESP because its size is estimated to be one-hundredth that of the ESP.

Reduced Costs of Recycling

In the steelmaking industry large amounts of particles are entrained in the furnace flue gas. In electric arc furnaces 1% to 2% of each charge is converted to dust (Herlitz and Baumann 1987). In the past this dust has been dumped, but now it is listed as a hazardous waste. If this dust could be recycled, the hazardous waste disposal problem would be eliminated. The dust also has commercial value because of its alloy content. The agglomerator could reduce the cost of recycling this material by increasing the average particle size.

Decreased Health Hazard

As Figure 8.2 shows, the collection efficiency of submicron particles is quite poor. For particles 1 micron in diameter or less, an ESP with average efficiency, which is typical in the industry, will capture less than 90%. Unfortunately, these particles create a significant health hazard because they can enter the respiratory system. The agglomerator will allow conventional filtration devices to remove a greater percentage of the fine respirable particles.

8.2.3 Technical Feasibility

The technical feasibility of the agglomerator was analytically investigated by calculating the charge delivered to the particles, the forces pulling the particles together, the trajectory and time required for agglomeration, the interparticle adhesion forces, and the force necessary to pull apart agglomerated particles. These issues are addressed below in the order that a particle moves through the electrostatic agglomerator (i.e., charging, electrophoresis, adhesion, and agglomeration).

Charge Delivery - Ion Bombardment and Diffusion

The easiest method of charging gas-suspended particles is with a corona discharge. A corona can charge particles in one of two ways: ion bombardment and ion diffusion. Calculations show that for particles larger than 1 micron ion bombardment is the dominant effect, and for submicron particles ion diffusion dominates.

For previously uncharged particles, Moore (1973) and Straus (1971) determined that nearly 90% of the attainable charge is reached in the first millisecond. About 10 msec of ion bombardment is needed for the particle to reach 99% of the maximum charge. This analysis indicates that it is quite feasible to adequately charge the particles.

Interparticle Forces, Trajectories, and Time to Agglomerate

The interparticle forces are electrostatic in nature. Therefore, they are a function of the inverse of the interparticle distance raised to power of 2 (or 5 if polarization effects are considered). For a typical coal-fired device, interparticle separation distance is calculated to be less than 1/2 mm. At this distance the major electrostatic forces between two charged particles is the Coulomb force (F_c). The force from polarization of the particles, which exists even if only one of the particles is charged, is two orders of magnitude lower.

In addition to the interparticle forces there are forces on each particle from the electric field between the high voltage negative and positive wires. For an electric field of 10^5 V/m, the magnitude of the applied force (F_E) on 10-micron and 1-micron particles is 8×10^{-11} N and 8×10^{-13} N, respectively. The corresponding acceleration of 1-micron particles is about 140 times that of the earth's gravity.

The particle trajectories were examined to determine the time required for the two particles to come into contact from the initial maximum separation distance. This examination was done by obtaining an approximate solution to differential equation of motion, including the inertial and aerodynamic forces. The resulting relative velocity of the two particles approaching each other is 5 to 6 cm/sec, resulting in closing times of 0.01 second. This is not a surprising result. Similar velocities are experienced in conventional electrostatic precipitators. However, the electrode separation, which is half the distance a particle must travel to precipitate, can be as much as 3 orders of magnitude larger than the distance the particles must travel to agglomerate. This has obvious implications on the equipment size and, hence, the cost. For many older coal-burning power plants, the question of size may be more important than cost because the plants do not have enough space to install additional large-scale pollution control equipment.

Interparticle Adhesion Forces and Collisional Effects

When two oppositely charged dielectric particles come into contact, they adhere to each other because of the following forces:

1. interparticle Coulomb force
2. force due to polarization (dielectrophoretic)
3. van der Waals force
4. surface tension/capillary force.

For aerosols the capillary force will be the dominant force. It may also become important for solid particles coated with moisture or condensing acids, which may occur under power plant exhaust conditions. It can be shown that for dry particles the van der Waals forces dominate the electrostatic forces even if the "point of contact" electric field enhancement and, hence, Coulomb force enhancement analyzed by Moslehi and Self (1984) is taken into account. Calculations show the van der Waals adhesion force is of the order 10^{-7} to 10^{-8} Newtons.

Having established that agglomeration of particles is feasible, the forces that may break the agglomerate apart must be examined. The most likely cause of agglomerate separation are mid-stream particle/agglomerate collisions. For example, in a system of 3 particles, particle 1, with a mass m_1 , moves at a relative velocity v_1 toward an agglomerate of m_2 and m_3 . Upon impact, the mass m_2 transfers most of the m_1 momentum to m_3 . We seek the relative velocity v_1 of mass m_1 that can impart sufficient acceleration to m_3 to cause its separation from m_2 . Assuming that particles 1 and 2 are 10 microns in diameter and that particle 3 is a 1 micron particle, the acceleration is

$$dv_3/dt = 2.5 \times 10^8 v_1$$

To overcome the van der Waals adhesion force (10^{-7} to 10^{-8} Newtons), the necessary acceleration of m_3 is about 8×10^6 to 10^7 m/sec². From the above equation, this yields relative velocity v_{rel} /sec. It is highly unlikely that this relative interparticle velocity can be achieved in a viscous media such as air. Therefore, particle-to-agglomerate collisions are not likely to overcome the van der Waals forces and break up the agglomerate.

Summary

The following conclusions can be drawn from the above theoretical investigation:

- The particles can be adequately charged quickly with an acceptable agglomerator size.
- The charged particles are accelerated towards one another at 5 to 8 cm/sec, resulting in closing times of 0.01 second.
- Van der Waals forces will adhere particles together.
- Collisional forces will not separate previously adhered particles.

8.2.4 Impediments to Wide-Scale Use

While the agglomerator appears to offer considerable advantages, the technology needs to be developed and a full-scale demonstration is needed for industry acceptance. Specifically, the following needs to be done:

1. Small-scale experiments must be performed to demonstrate the concept's feasibility.
2. Agglomerator operating conditions must be parametrically analyzed. These conditions include particle charging, forces pulling the particles together, the interparticle adhesion forces, and the force needed to pull apart the particles. The equations describing these physical phenomena have already been written, and some approximate solutions have been obtained.
3. The agglomerator's energy consumption must be accurately determined. This is influenced by particle loading and size distribution, the channel aspect ratio, whether staging is used, the agglomerator size, and the gas and particle makeup.
4. A subscale test in an industrial environment must be conducted to demonstrate the technology to the end users. A technology demonstration that uses a slip stream of a typical, large plant would be ideal.

8.2.5 State of the Art of Competing Technologies

The proposed concept is unique and, as far as we know, not studied in the context of the present application. However, many studies have been conducted on the same principles of particle-to-particle attraction/repulsion in other applications. In some cases the objective is to avoid agglomeration and particle stringing (forming chains); in other cases, the objective is the opposite. For example, Wolny and Opalinsky (1983) added a small proportion of fines (0.1 vol %) to 1 mm polystyrene beads to neutralize the charge on the beads and to prevent their adhesion to the walls of a drying fluidized bed. Thus, in this successful application their objective was the same as ours to agglomerate fines on larger particles.

One of the most troublesome difficulties in electrostatic coal beneficiation is the suspected agglomeration of fine ash on oppositely charged coal particles. The proposed concept in part originated in my attempts to prevent such agglomeration.

With the exception of the ESP, the conceptually nearest relative to the agglomerator is an electrofluidized bed (EFB). Zahedi and Melcher (1976) proposed its use as a submicron filtration device. In the EFB, the large bed particles form the collection sites of the submicron particles flowing through the bed. The inertial impaction filtration present in nonelectrified beds is enhanced and is dominated by the electrostatically induced filtration because of an imposed electric field across the fluidized bed. Experimental work confirmed 98% collection efficiency of submicron particles.

An example where agglomeration or particulate chain formation is the objective are devices that use electro-fluidized beds for momentum transfer, such as special clutches or brakes. Fundamental study of the momentum transfer was carried out by Dietz and Melcher (1978).

Particle/fly ash acoustic agglomeration research is being conducted at the Pennsylvania State University. However, current predictions show operating costs of this system to be as high as \$550,000/year for a 250-MW power plant (Reethof 1985).

ESPs and baghouses can be used to remove fine particles. However, the capability of these devices in capturing the smallest particle diameters is limited. A medium-efficiency ESP has a 90% capture efficiency with particles sizes no smaller than 5 microns. Cyclones, while less expensive, have a 95% capture efficiency with particles no smaller than 40 microns. A fabric filter has an efficiency in the high nineties down to a particle size of 1 to 2 microns. However, its capital and operating costs are high. Of course, it is possible to derate a given industrial process. This reduces particulate emission at all sizes but it also reduces production.

In the glass industry electrical boosting can be added to a furnace, thus allowing, for a given production level, less combustion gas flow and reduced particulate carryover. However, electrical boosting significantly increases the operating cost of a furnace, primarily because of the high cost of electricity in most parts of the country.

8.2.6 Market Potential

The market potential for the agglomerator is quite large because many industrial processes have large amounts of particulate emissions. Table 8.1 lists several industrial sources (Shannon 1971). For example, in the steel industry alone, about 500 furnaces ranging in capacity from 400 to 2400 tons per day could benefit from using the agglomerator. Likewise, in the glass industry about 250 furnaces ranging in capacity from 150 to 600 tons per day could benefit from using the agglomerator.

8.3 FUTURE CONCEPT DEVELOPMENT

The next steps in the agglomerator's technical evaluation are as follows:

- bench-scale testing to verify and refine the theoretical model
- system study to determine all of the components needed and their interrelationship and to identify the optimum configuration of the agglomerator and auxiliary components for various market niches.

TABLE 8.1. Fine Particulate Emissions from Industrial Sources
(less than 3 microns) (10³ tons/year)

Industrial Source	Particulate Emissions
Coal - Electrical Utility	970
Iron and Steel	300 to 570
Pulp Mills	319
Cement	177
Carbon Black	93
Secondary Non Ferrous	127
Glass	16 (a)
Municipal Incinerators	10

(a) Estimated by author.

- subscale or pilot demonstration in an industrial or power plant environment to obtain durability and maintenance information for optimizing the equipment's operational aspects (with end-user's participation) and to demonstrate the technology to industry
- market study to determine which niches are most favorable for the agglomerator and business plan development to commercialize it.

A two-phase program is recommended that will address all of the above issues.

8.3.1 Phase I - Near-Term Development

A bench-scale experimental facility, as shown in Figure 8.5, will be constructed and operated. It consists of a Plexiglas^(a) enclosure containing the inlet plenum (top), the charger section, channels, agglomeration section, and a cylindrical section that will be used as a particle drop-out chamber and a flow discharge plenum before the particles' entry into the indicated cyclone.

A laser particle sizer will monitor the particulate number density and their size distribution, traversing from the charger inlet position to the agglomerator section exit. The working fluid will be room temperature air provided by a centrifugal blower or mixture of N_2 and CO_2 stored in gas cylinders. The flow rate through the electrostatic agglomerator (nominally 50 cfm) will be controlled by bleeding off the excess air provided by the oversized blower. The particles will be introduced into the main gas flow by a fluidized bed feeder. The particles will be SiO_2 and Al_2O_3 used in the optical grinding industry and comminuted fly ash purchased from a local pulverized coal-fired power plant.

After the flow passes through the agglomerator, it enters a conventional cyclone. The cyclone discharge will be sampled using a high-density filter to collect the particles and subsequently determine the particulate size and number density exiting the system. However, because the cyclone is not the subject of this study, the data of

FIGURE 8.5. Proposed Experimental Facility for Testing the Electrostatic Agglomerator

(a) A trademark of Rohm & Haas, Philadelphia, Pennsylvania.

primary importance must come from the laser particle sizers. The lasers will determine if the particles are agglomerating and how large the agglomerates are.

The results from the bench-scale testing will be used in refining the conceptual design and designing the full-scale system. Also, in this phase the target industrial or power plant market will be identified. The best market niche for the agglomerator will be useful in determining host site candidates and the final design details for a full-scale demonstration.

Phase I will also include a preliminary evaluation of the commercialization approach, and various marketing partner candidates will be identified. These candidates will probably be ESP or cyclone manufacturers with close ties to the targeted market niche. The marketing partners will be chosen in Phase I so that they can contribute their expertise in Phase II.

Consideration will also be given to producing the agglomerator. If internal resources and company overall plans permit, the Busek Co., Inc., may manufacture the agglomerator. Otherwise, a manufacturing partner will be sought.

8.3.2 Phase II -- Long-Term Development

The full-scale demonstration of the agglomerator will be accomplished in Phase II. A host site will be secured from the candidates identified in the previous phase. The agglomerator and auxiliary equipment will be designed and manufactured or purchased as necessary.

The equipment will be operated at the host site and data collected to document its performance. The facility will also be available for tours by prospective end users. Concurrent with the demonstration task, the final marketing approach will be determined and a business plan written.

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9.0 LARGE-SCALE GENERATION OF MICROBUBBLES TO IMPROVE FLOTATION PROCESSES AND TO SAVE ENERGY

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ABSTRACT

Low-cost efficient methods of producing microbubble dispersions on a large scale need to be developed to take advantage of many potential industrial applications where microbubble dispersions could significantly reduce energy consumption and the cost of industrial separations processes. Colloidal gas aphrons (CGAs) are a stabilized form of microbubble dispersions that contain 50% to 70% of 50+/-40 micron diameter bubbles in water-based solutions. They have many potential applications, such as enhancing bioreactions, fine particle flotation, in situ hazardous waste treatment, and even firefighting.

Laboratory-scale experiments on CGA applications have used spinning discs to produce microbubble dispersions in small quantities. However, the spinning disc method may have limited potential for economical scaleup. A packed column method has been demonstrated for producing larger quantities of CGAs. A spinning cylinder currently is being tested as an alternative method for economically producing large quantities of high-quality CGAs. Preliminary results of bench-scale tests on the spinning cylinder indicate a considerable improvement in generating microbubbles with good stability and bubble size, minimum void air, and reasonable operating costs. A larger unit has been designed and is being built for testing in this project.

The first objective of this work was to scale up, design, fabricate, and test a 30 to 50 gal/min spinning cylinder generator. The goal was to make the equipment available for conducting feasibility/economic field studies for several applications. The second objective was to test the existing pilot-scale generator using various spinning cylinder configurations to optimize the system for maximum flexibility.

9.1 INTRODUCTION

Foams generally fall into one of two classes: "wet" and "dry." In a wet foam the air content is low, 75% or less, which allows the bubbles to be far enough apart that none of them is distorted by another. As a result, the bubbles adopt a spherical shape in an attempt to minimize their surface energy.

The traditional term for a wet foam is kugelschaum or spherical foam. The diameters of the bubbles of a kugelschaum are not limited to any particular size; however, there are some differences between foams consisting of mostly tiny bubbles and foams consisting of mostly large bubbles. The greatest difference is in the time the bubbles stay in suspension. As bubble size decreases, the force driving the bubbles to the surface (buoyancy force minus drag force) also decreases, thus lengthening the amount of time it takes for the bubbles to rise to the surface. They remain in suspension longer. Kugelschaums with bubble diameters less than 250 microns are termed microbubble foams and, because of their size, are more stable than the larger (up to several millimeters) kugeischaums.

Generating bubbles is not necessarily the precursor to foam generation. Bubbles, large or small, can be generated and exist widely dispersed in a continuous medium. These formulations have very low concentrations of air and are usually transitory. Examples include bubbles formed by electrolysis or dissolved air techniques (10% air bubbles).

As bubble size is reduced to below 50 microns with few greater than 100 microns, colloidal properties become apparent such as the ability to remain dispersed in liquid without significant coalescence. These 40% to 60% microbubble foams contain a dispersion of small stabilized air bubbles in an aqueous medium. They have a viscosity of 10 centipoise (cp), reducing of course, to that of water as the quality (good stability and bubble

size and minimum void air) approaches zero. First investigated by Sebba (1971) under the name of microfoams, their behavior was significantly different from other foams; to prevent confusion the name "colloidal gas aphron" was introduced (Sebba and Barnett 1981).

The name "aphron" comes from the Greek "αἴψωρ", a foam, and has been coined to mean any fluid encapsulated in a thin aqueous shell, or, a true bubble. Like microbubble kugelschaums, CGAs consist of gas spheres enclosed in a soap film of dilute surfactant solution; the major difference in the two lies with the stabilized encapsulating soap shell characteristic of CGAs. CGAs of practical interest typically contain 50% to 85% air by volume. As the concentration of air is increased above or below this range, this stabilized microbubble foam demonstrates reduced effectiveness in most applications.

Although Sebba (1981) lists the size range of CGAs at 25 to 50 microns, samples taken by the improved technique developed in this work indicate that the range is broader, 15 to 120 microns, with an average of 50.7 ± 22.7 microns. Further technical aspects of CGA structure and properties are discussed in Sebba (1981) and in a recent book by Sebba (1987).

9.2 CONCEPT ASSESSMENT

In the following sections, the proposed concept is described, and its potential energy savings, technical feasibility, impediments to widespread use, and prior work and state of the art are discussed.

9.2.1 Description of the Concept

A large generator has been designed to produce CGAs at a rate of 30 to 50 gallons per minute. The design is similar to the small cylinder CGA generator shown on Figure 9.1. Details are not included because of patents currently being filed. The generator has been designed to operate at 100 psig and will have an all 304 stainless steel construction. The outer stainless steel 12 inch shell and inner spinning cylinder can be replaced with clear acrylate piping to reduce weight and potential balance problems, and to allow visual observation while it is operating near atmospheric pressure. At this time the materials have been received and fabrication is proceeding.

The design will allow a wide range of rotational speeds ranging from 587 rpm to as high as 5280 rpm. Based on scaleup from earlier testing using a smaller-diameter cylinder, 1250 rpm should provide the same surface

FIGURE 9.1. Spinning Cylinder CGA Generator

shear. The critical design and fabrication factors will be the weight balance of the spinning internal cylinder and the alteration of the internals to maximize production of an acceptable microbubble dispersion tailored to satisfy a particular application.

9.2.2 Potential Energy Savings

Using microbubbles for flotation has potential because they are easy to generate and have high quality (bubble concentration), good stability (slow coalescence), and limited void air. The first application of a method for producing commercial quantities of fine microbubbles could be for improving flotation or separation of wastes containing natural surfactants. Foaming could be achieved using a low surfactant concentration of 100 to 300 parts per million (ppm) with the packed bed generator, a device recently fabricated for generating microbubble foam (Suggs 1987) (see Section 9.2.5). Therefore, wastewater treatment (flotation) of food wastes, textile waste, perhaps paper wastes, and oily wastes from the metal cutting industry (aluminum, steel) are possible applications. In those treatments, little or no surfactant should have to be added.

Other flotations of phosphate slimes, algae (harvesting), inorganic fine particulate, and coal beneficiation flotation have also been addressed successfully in the laboratory. In commercializing those applications, a surfactant most likely would have to be added for processing.

An improved flotation technique will be accepted if technical improvements can be made and its economics justified. In waste treatment, the amount and costs of subsequent biodegradation will be reduced if fine particles and dispersed oils can be removed and recovered. Improved pretreatment to remove particulate matter would also reduce the probability of hazardous refractory organics being carried through into secondary treatments and concentrating in the sludges. Therefore, both ease operation of secondary waste treatment and cleaner sludges for soil conditioning rather than landfilling could result.

Microbubble technology could have its greatest energy savings' impact in biological systems. The primary application would be in improved, energy-efficient oxygen mass transfer for applications ranging from biological reactors (ordinarily a naturally foaming broth) to activated sludge processing (using a foaming waste stream). A recently completed M.S. thesis (writing stage) in our laboratory has clearly demonstrated considerable improvement in biological growth using CGAs with much reduced agitation (energy savings). The dissolved oxygen in the reactor stayed much higher, and no surfactant had to be added. Any continuous CGA generator would have considerable application in this field and would have wide application in many biological systems where mass transfer of oxygen to a viscous broth is limiting.

The major cost in operating activated sludge processing plants that treat both sanitary and industrial waste is the enormous electrical cost for beating (sparging) air into the system for biodegradation to occur. The larger 1000 to 3000 micron bubbles generated have a very high rising velocity but a very low utilization, about 8% to 15%. A pilot unit capable of generating large quantities of microbubbles ranging in size from 25 to 100 microns offers an option for those plants. Smaller bubbles provide much higher retention and result in utilization well above 50%. The rising velocity is proportional to the bubble diameter squared. However, the application would be restricted to systems having some foaming characteristics, such as certain feed streams and in-process streams.

An even larger market is the biodegradation (secondary treatment) of industrial and domestic sewage. Because CGAs have a strong tendency to be retained in saturated soil matrices, considerable testing has been under way to prove the feasibility of using CGAs to supply oxygen for biodegradation in the saturated zone (Michelsen, Wallis and Sebba 1984a, 1984b; Michelsen, Wallis and Lavinder 1985; Michelsen, Wallis and Sebba 1986). That application would compete with sparged air and hydrogen peroxide addition processes and groundwater injection/recovery techniques. Currently, costs for providing oxygen using CGAs do not compete with sparged and surface aeration techniques found in activated sludge treatment processing even assuming complete 100% oxygen use of all air formed into CGAs. However, where stripping of toxic volatiles from activated sludge processing is a

concern and where activated carbon adsorption of vent fumes is contemplated, a closed system using reinforced (high O_2) air for generating CGAs and subsequent biodegradation could prove technically feasible and economically acceptable.

In the new biotechnology areas, the use of small microbubbles for separation (flotation) of impurities could offer long-term opportunity for CGA utilization. With proper bubble formulation, selected adsorptions and separations may be possible.

Using CGAs offers several other opportunities for saving energy. In aluminum slimes' processing, CGAs have been demonstrated to enhance the recovery of an enriched aluminum cut for recycle. Landfilling costs and bauxite processing could be reduced if a greater percentage of aluminum could be recovered from ore. Similarly, using flotation to reduce sulfides and ash from finely crushed coal has received considerable attention and looks promising. The scaleup of CGA generation should provide bench-scale testing capability of the surface chemistry for separations and capacity for large-scale field testing. The change in U.S. energy needs to a natural resource such as a fine coal ground and floated to remove sulfur and ash represents an appealing answer to environmental and balance-of-trade problems.

9.2.3 Technical Feasibility

While the proposed generator is being fabricated, testing is continuing on several of the first-generation spinning cylinder modifications, shown in Figure 9.1. The test results with a uniquely designed cylinder "E" and internals are shown in Table 9.1. As the table shows, both rotameters were calibrated to indicate liquid and air rates. An inverted bucket was used to calibrate the air rotameter. The total dispersion production was determined by collecting the final dispersion at atmospheric pressure and measuring the volume collected during a 1-minute interval. The rpm of the spinning system was measured using a tachometer. The stability, H' , is determined by taking a 250 ml sample of the product dispersion into a standard 250 ml graduate. Direct weighing provides the basis for determining the quality, and the volume of the clear liquid after one minute of bubble rise provides the basis for measuring stability.

Earlier studies by Suggs (1987) have shown that by correcting H' to a percentage of total rise (all bubbles coalesced), this corrected H' or stability can be correlated as a function of quality. The higher the quality, the lower the H' (better stability). The air utilization is an important determination because it provides a measure of the total air actually formed into microbubbles. The large void air, G , passing through the generator could interfere with the microbubble performance in most applications.

The power consumption was determined by placing a known low resistor in series with the lead to the router used for testing and measuring voltage over both the resistor and the motor. With these measurements, the wattage used by the router was determined. The energy necessary to produce one liter per minute of microbubbles (the product desired) was then calculated. Finally, the liquid in the dispersion was determined by multiplying the total dispersion production by (one minus the fraction product quality). Comparison of this calculated water rate to the calibrated rotameter liquid rate provides a closure on the liquid material balance.

Figures 9.2, 9.3, 9.4, and 9.5 plot key information from testing conducted using cylinder "B." The air rate was kept constant during all these tests. Figure 9.2 shows that increasing water rate results in lower stability (increased H'). Also, the H' can be lowered by increasing the rpm, shown in Figure 9.3, but with a sacrifice in greater power input. To secure good air utilization, an increased water supply is needed, as shown on Figure 9.4. Also, as water rate is increased, the quality also increases, strongly indicating that turbulence and shearing have been enhanced to produce a higher air concentration but with little change in power per quantity of air formed as microbubbles. Figure 9.5 shows that utilization decreases with rpm. At a high rpm, the centrifugal force most likely throws the liquid out toward the wall and mixing is impaired. High rpm produces good microbubbles but has poor utilization and high energy demand. A higher foam quality (air to liquid mixture) can be produced but results in larger bubbles (H' greater) as water flow rate increases with constant air supply.

TABLE 9.1. Microbubble Generation Using Spinning Cylinder "E"

Run No.	Rotameter Air Rate L/min.	Rotameter ^(a) Liquid Rate L/min.	Total Dispersion Production L/min.	RPM	Stability ^(b) H ¹ , mL in. One min.	Quality Percent Air in Total Dispersion	Utilization ^(c) Percent Air in Forming Dispersion	Power Consumer Watts	Power per ^(d) Microbubbles Generated Watts/(L/min.)	Liquid in Dispersion Production, L/min.
E1	13.8	4.1	16.4	5000	7.0	71.0	85.6	149.6	12.85	4.7
E2	13.6	8.3	18.8	5400	7.5	88.5	94.7	183.7	14.26	5.9
E4	13.6	6.8	20.0	5000	12.5	64.5	95.0	147.7	11.45	7.1
E6	13.6	8.1	20.0	5000	14.5	62.0	91.2	168.5	13.59	7.6
E7	13.6	10.2	23.2	5000	25.5	56.5	96.4	168.0	12.82	10.1
E3	13.6	6.8	19.8	3400	18.5	66.0	95.1	91.2	7.05	6.64
E5	13.6	6.8	19.9	7000	7.5	65.5	95.8	318.7	32.65	6.87
E8	13.8	10.2	24.8	3000	47.0	57.0	103.0	87.8	6.23	10.7
E9	13.8	10.2	24.8	7000	10.5	55.5	101.0	332.1	24.14	10.8

(a) Tap water contains 400 ppm sodium dodecyl benzene sulfonate.

(b) Stability, H¹, is mL of liquid phase separation one minute after filling standard 250 mL graduate.

(c) Utilization is dispersion production x quality/rota air, eq (E1) $16.4 \times .71/13.6 = 85.6\%$.

(d) Power per production of microbubbles eq (E1) $149.6/(16.4 \times .71) = 12.85$.

FIGURE 9.2. Stability as a Function of Liquid Flow Rate ('B' configuration)

FIGURE 9.3. Stability as a Function of RPM or Spinning Device ('B' configuration)

Figures 9.6, 9.7, 9.8, and 9.9 show the results of testing with the spinning cylinder 'E' configuration; see Table 9.1 for details. Again, increasing flow results in decreased H' , meaning that bubble size is diminished. However, air utilization remains flat across the entire range; and quality, while dropping as flow rate increases (see Table 9.1), was significantly higher than testing with the B configuration. Also, rpm had little influence in utilization although stability was poorer, using only 3000 rpm.

In summary, the 'E' configuration significantly improves the generation of a microbubble dispersion with lower energy inputs. Of particular importance is the relatively constant air utilization over a range of operating conditions. The energy inputs, while believed to be comparable (precise) between runs within the B and E sets, may not be accurate. The standard low OHM resistors that were used drifted from set to set.

FIGURE 9.4. Air Utilization (microbubbles formed) as a Function of Liquid Flow Rate (*B* configuration)

FIGURE 9.5. Air Utilization (microbubbles formed) as a Function of Spinning Device (*B* configuration)

9.2.4 Impediments to Widespread Use

Generating a large quantity of a microbubble dispersion containing 25 to 110 micron bubbles appears to be technically feasible. However, to produce these microbubbles, some source of natural and/or additional surfactant (100 to 500 ppm) must be present to lower the surface tension in order to form and stabilize the microbubbles. Also, a greater energy input is required to generate the expected dispersion, partly because of the viscosity of the dispersion generated. Using a spinning cylinder viscosimeter, the observed viscosity of the 40%, 50%, and 60% dispersion (percentage of microbubbles dispersion) was 10 cp but increased to 30 cp at a 70% microbubble dispersion. Therefore, efforts must be directed at optimizing microbubble production and minimizing energy input and raw material (surfactant) cost.

9.2.5 Prior Work and State of the Art

Gas aphrons were first produced in the laboratory by Sebba (1971) using the venturi method. This method essentially depends upon the fast flow of a dilute surfactant solution past a venturi throat, at which point there is a provision for entry of the gas, under about one atmosphere excess pressure, through a very narrow channel.

Several years later, Sebba (1985a) developed an improved technique for producing CGAs: the spinning disk. That method uses a small disk rotating in excess of 4000 rpm between two carefully positioned baffles in a

FIGURE 9.6. Air Utilization (microbubbles formed) as a Function of Liquid Flow Rate ("E" configuration)

FIGURE 9.7. Air Utilization (microbubbles formed) as a Function of RPM of Spinning Device ("E" configuration)

container filled with dilute surfactant solution. Since the introduction of the spinning disk technique and its ability to generate CGAs at 4 L/min, no other generating techniques have been tested. The advent of this colloidal system and the ways of generating it opened up new avenues for separation techniques and provided new solutions to old problems. Sebba (1985b) has identified the following applications:

- stripping of dissolved gases from water
- removal of finely dispersed oils from water
- ion and precipitate flotation
- removal of ash forming materials from coal
- removal of oil from sands
- flotation of microorganisms such as algae and bacteria
- oxygen transport to subsurface matrices.

Unfortunately, generation techniques have been limited to producing only small amounts of CGAs. However, all of these applications, if commercialized, would require much greater quantities of a microdispersion of air bubbles in water. Because of this demand, a technique for generating "commercial" amounts of CGAs is needed. Scaled-up versions of the venturi and batch spinning disk methods should meet the requirements, but have not been successful. Sebba (1985a, 1985b) ruled out the possibility of scaling-up the venturi technique.

FIGURE 9.8. Stability as a Function of Liquid Flow Rate ("E" configuration)

FIGURE 9.9. Stability as a Function of RPM of Spinning Device ("E" configuration)

Recently, Suggs (1987) designed and fabricated a portable pilot unit for generating microbubble foam and tested a packed bed generator device using glass spheres. This technique has produced large quantities of good CGAs with bubble size distribution approaching those produced with a spinning disk. Figure 9.10 shows a schematic of the pilot plant unit that will be modified to replace the packed bed with a spinning cylinder device.

Suggs' studies also have led to standardization of several methods for rapidly determining CGA characteristics. The stability of the CGAs is determined by following the rise velocity of the liquid phase as the bubbles are placed in a standard 250 ml graduate cylinder. Also, by placing a small cell on a microscope, Suggs has quantified bubble size distribution from photographs of the video display. The sample line shown on Figure 9.1 was the continuous source of microbubbles flowing through the cell. The flow was turned off during photographing. The research continues on using CGAs for in situ treatment of hazardous waste, and fundamental or CGA transport through soils.

A recent laboratory study has been completed using CGAs for flotation of fine particulates. One unpublished study on suspended fine particulates (clay) at the 30 ppm level showed that CGA flotation could remove 95% of the suspended matter while dissolved air flotation removed only 50% using the same air volume for flotation. A

FIGURE 9.10. Portable Pilot Unit for Generating Microbubble Foam

second study by Lohse (1986) has clearly demonstrated the ability of CGAs to float algae effectively in a countercurrent flotation chamber design.

A pilot flotation cell (tank) 6 ft long, 1 ft deep (front to back) and 4 ft high has been designed and constructed to test the scale-up feasibility of using CGAs for removing contaminants from water. Several test runs were made in the Chemical Engineering Unit Operations laboratory determine if the flotation tank and CGA generation system would function properly. The tests indicated that the flotation tank performed well and that CGAs could remove suspended particles from contaminated water in larger-scale testing.

Figure 9.11 shows the proposed CGA generation configuration for field testing. This system can easily be changed for dissolved air flotation performance operation. Any field testing to be conducted will most likely include particulate or oil flotation using a portable flotation tank having the same dimension as the pilot cell.

9.3 FUTURE DEVELOPMENT OF THE CONCEPT

Commercial testing at the following facilities is being negotiated. One of the two following tests will be conducted:

1. In situ testing using pilot quantities of CGAs as a direct replacement may be conducted at a turkey processing facility near Harrisonburg, Virginia. The other option is to take a side stream and test flotation in the pilot flotation cell described earlier and compare performance with the existing flotation system. CGAs would be supplied by the pilot CGA generator.
2. Testing may be conducted at a Reynolds metal aluminum fabrication facility in Charlotte, North Carolina. The possible arrangements are similar to those described above except that CGA generation would probably require the addition of some sodium dodecylbenzene sulfonate to assure that stable microbubbles are generated.

FIGURE 9.11. Flotation Cell and CGA Generation System

9.4 REFERENCES

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10.0 APPLICATIONS OF A MAGNETIC CYCLONE

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ABSTRACT

This concept addresses two potential applications of a magnetic cyclone. The first application examines and demonstrates improved recovery of fine magnetite. The fine magnetite used in conventional dense media plants for coal cleaning is not fully recovered and recycled. The project results show that the magnetic cyclone can recover dense media magnetite (as purchased by operators of dense media coal cleaning plants) effectively without excessive magnetic fields or feed pressures. However, when samples from process streams of coal cleaning plants were used, the recoveries were lower than with pure magnetite, largely because of the very fine size of the magnetic particles in the process streams. Additional tests will examine cyclone geometry and magnetic field variations to further improve the magnetic cyclone recovery of these fine particles.

The second application concerns dewatering of steel plant sludges to allow these iron-bearing materials to be disposed of or reused. To date a literature search has been undertaken to determine the characteristics and potential of this application. Unfortunately, appropriate plant samples were not available in time to complete the research, but tests should be finished by the end of April 1988, when a final report will be made available.

10.1 INTRODUCTION

The scientific concept of combining magnetic forces with classification forces within a hydrocyclone was investigated in New Zealand about ten years ago by Dr. J. L. Watson for possible use in beneficiation processes. This work is reported in a master's thesis (Hiew 1980). The intended use of the device was the separation of titanomagnetite from gangue minerals in an iron sands mining operation.

Traditionally, such beneficiation has been conducted using separate magnetic and gravity processes in series (Watson 1978; Watson and Low 1982). Using the magnetic cyclone in that application was found to be very limited because of the relatively coarse size of the sands, ranging between 100 and 600 microns. The difficulties encountered included the generation of a magnetic field gradient, across a cyclone, of a sufficient size to permit separation of the sands. Problems also were encountered in the laboratory with handling the large flow rates needed to operate a cyclone of this size.

Commercialization of the magnetic cyclone appears to depend on successful demonstration of process applications for the concept. This project targeted two specific applications for research and investigation:

- recovery of magnetite dense media in dense media coal cleaning plants
- recovery of solids from waste sludges in the steelmaking industry

Both applications involve materials that have particle sizes generally less than 50 microns in diameter and that exhibit a strongly magnetic character. The proposed processes are essentially solid recovery techniques.

10.2 DESCRIPTION OF THE CONCEPT

The scientific principle of the concept of the magnetic cyclone is well established (Watson and Amoko-Gyampah 1983; Fricker 1985). It involves the use of magnetic force in a radial direction across a cyclone,

where existing centrifugal, viscous, and gravitational forces act on particles in a fluid. The fluid used to transport the particles into the cyclone may be air or water, with water being the prime medium in mineral processing operations.

A hydrocyclone is a device that permits particles in water (pulp), fed tangentially, to be separated according to size and density. Figure 10.1 illustrates the essential forces involved in the separation. Centrifugal forces compete with viscous drag forces to determine whether a particle will exit the cyclone through the spigot (underflow) or vortex finder (overflow). If a particle reaches the cyclone's outer wall, it will discharge through the spigot as underflow, which contains the coarser material. On the other hand, if the water drag forces pull the particle towards the center of the cyclone, it will be discharged through the vortex finder as overflow, which contains finer material.

The separation size, or d_{50} , of a cyclone is dominated by the cyclone radius because of its importance in calculating centrifugal force. To achieve a separation size of greater than 75 microns, a cyclone of at least 50 cm diameter typically is required. To achieve a separation size of less than 40 microns, the cyclone diameter must be reduced to 10 cm or smaller. Although the cyclone's cylindrical diameter has the major influence over the separation size, both increasing flow rate and particle density will decrease the separation size, while an increasing pulp viscosity will increase it.

Recovering particles finer than 25 microns to the spigot is very difficult, as shown in Figure 10.2, where a classification curve plots the fraction of each size range reporting to the spigot product. This curve represents data for recovering magnetite (Fe_3O_4) in a 7.5 cm aluminum cyclone (Watson and Amoko-Gyampah 1983). As the figure shows, the separation size is 35 microns, and below 10 microns as little as 10% may be recovered to the spigot. The remainder flows to the vortex finder product, along with most of the water.

In many applications the recovery of particles finer than 10 microns is important and is achieved, at the expense of throughput, by using very small-diameter cyclones. One such cyclone is a multicyclone (2.5 cm dia.), which is used in gas cleaning or dedusting. If the particles are magnetic, a magnetic force can be used, in addition to existing forces, to attract the particles to the outer wall of the cyclone and hence to spigot

FIGURE 10.1. Force Illustration for Conventional and Magnetic Cyclones

FIGURE 10.2. Classification Curves for Conventional and Magnetic Cyclones

recovery. Figure 10.1 shows, in addition to the classification forces, these magnetic forces superimposed on a particle in a hydrocyclone. Reinforcing outward radial forces decreases the separation size and therefore recovers finer material to the spigot.

The classification curve of a 7.5 cm diameter magnetic cyclone is also shown in Figure 10.2. The effect of adding a magnetic force to this cyclone for treating magnetite is dramatically evident (Watson and Amoko-Gyampah 1983). The separation size decreased from 35 microns to less than 10 microns when the magnetic field was applied, indicating that the magnetic cyclone has considerable potential in treating fine magnetic materials.

In both of the proposed applications, it is important to recover as much of the magnetic material as possible in the spigot product. To do this, the magnetic field must be of sufficient strength and field gradient to move fine particles to the cyclone wall. Previous work has suggested that for ferromagnetic materials, such as magnetite, the field strength need not exceed 500 gauss, but the field gradient should be in excess of 50 gauss/cm (Watson and Amoko-Gyampah 1983). Using these conditions as a starting point, the two proposed applications of a magnetic cyclone were investigated.

10.3 TECHNICAL FEASIBILITY

In this section, the concept's technical feasibility and experimental results are discussed. The setup and procedure for the test circuits are discussed first, followed by the results of experiments conducted to date on both applications of the concept.

10.3.1 Test Circuit Setup and Procedure

A 5 cm (2") polypropylene cyclone was purchased and mounted in a test circuit, as shown in Figure 10.3. The cyclone was fitted with 0.4 cm (0.125") spigot, but also had an adjustable rubber spigot, which allowed an outlet of 0.8 cm or less to be used. The magnetic field was provided by two permanent horseshoe magnets with gaps of 8 cm (3.2") and pole face areas of 18 cm X 11 cm (7" X 4.2"). The field strength in the gap of each magnet varied between 2 kilogauss, at 1 cm from the pole face, to 1.6 kilogauss in the center of the air gap. Typical field gradients within the air gap were 75 gauss/cm in the center and 200 gauss/cm at the top and bottom of the pole faces. Therefore, the cyclone was placed adjacent to the air gap to ensure a maximum field gradient. The circuit was operated at various pressure drops, but most tests used 6 psi. The sump was filled with water to

FIGURE 10.3. Laboratory Experimental Circuit

give a volume of 66 liters, with a typical solids loading of 500 g (1% solids). However, some tests used 5500 g of solid, giving a pulp density of almost 10% solids. The flow rate through the cyclone averaged approximately 30 liters/min at 6 psi, with a solids rate of 240 g/min at the lower pulp densities.

Three circuit configurations were used: 1) no magnet, 2) one magnet, and 3) two magnets. Figure 10.4 shows a plan view of the magnet/cyclone configuration; in the single-magnet mode the field gradient across the cyclone exceeds 300 gauss/cm.

10.3.2 Application 1 - Dense Media Magnetite Recovery

Unwanted minerals can be removed from mined coal by various techniques (Leonard and Mitchell 1988), but one very important method is dense media separation. In that process, shown in Figure 10.5, the coal is fed to a bath filled with a suspension of fine magnetite in water. The density of the suspension usually ranges from 1.25 to 1.50 g/cc. Because the coal is lighter than the suspension, the coal will float and the heavier gangue or waste minerals will sink.

FIGURE 10.4. Laboratory Magnet/Cyclone Configuration - Plan View

FIGURE 10.5. Typical Coal Preparation Circuit

It is vital to the operation of this process that the magnetite is recovered from the coal and the gangue mineral products for reuse in the bath. This is normally achieved by washing the magnetite off the products on screens, and then recovering the magnetite from the dilute pulp using drum magnetic separators. These separators use low-strength magnetic fields (less than 1000 gauss) resulting from permanent magnets placed within the drum shell. Obviously the magnetite is very fine to ensure a stable suspension. Table 10.1 gives a typical size distribution of magnetite purchased by operators of heavy media coal cleaning plants.

By using drum magnetic separators, most of the magnetite can be recovered, although some plants report magnetite losses as high as two to three kilograms per tonne of coal treated. A recent study by the Electric Power Research Institute (1987) estimated that 50 million tonnes of coal were cleaned by magnetite-based processes in 1985. This number is projected to rise to 285 million tonnes by 1990. Therefore, the loss of only few kilograms per tonne of coal treated can amount to many hundreds of thousands of dollars for a plant treating 1 million tonnes of coal annually.

Currently, U.S. supplies of magnetite are limited, and because it is not a high-priced product, transport represents a significant cost. The use of foreign supplies could result in higher magnetite prices, and therefore magnetite recovery processes represent an important area for dense media plants and merit further investigation.

Reference Tests with Pure Magnetite

To study the performance of the circuit, tests were initially conducted with pure magnetite, as purchased by heavy media coal cleaning plant operators. Three-circuit configurations were used at pressure drops of 8, 15, and 25 psi. The spigot diameter for these tests was 0.8 cm.

The test results are summarized in Table 10.2 for pulps of 1% solids and show that pressure only has a significant effect on magnetite recovery to underflow (U/F), when there is no magnetic field. As would be

TABLE 10.1. Magnetite Size Distribution

Size (microns)	56	28	14	7	-7
Weight %	3.2	37.5	39.5	15.5	4.3
Weight % Passing	96.8	59.3	19.8	4.3	-

TABLE 10.2. Circuit Variations and Pressure-Drop Effects on Magnetite Recovery

Circuit	Pressure psi	6		15		25	
		UF	OF	UF	OF	UF	OF
1 No Magnet	Wt(g)/5sec Weight %	16.8 85	2.9 15	27.8 88	3.9 12	36.3 91	3.8 9
2 One Magnet	Wt(g)/5sec Weight %	21.3 98	0.5 2	35.3 97	1.2 3	43.5 97	1.2 3
3 Two Magnets (N-N)	Wt(g)/5sec Weight %	16.7 82	3.6 18	35.5 98	0.9 3	42.2 97	1.5 4
4 Two Magnets (N-S)	Wt(g)/5sec Weight %	19.7 94	1.3 8	29.1 93	2.2 7	40.6 93	3.1 7

expected, when the pressure drop increases in this case, the recovery to underflow increases from 85% to 91% at 25 psi. In all other cases the recover appears to be independent of pressure and magnet configuration, with recovery to underflow being about 97%. The only major exception is where two magnets are used with opposite poles positioned adjacent to one another. In this case the recovery figures are reduced to about 93%.

At 6 psi, a single magnet can increase the recovery of magnetite from 85% to 98%. The size distribution data for tests 1 and 2 are given in Table 10.3. The size data illustrate that because the magnet has recovered more fine material, the underflow size distribution has become finer, while the overflow size distribution has coarsened. To test the effect of cyclone geometry on recovery, the 0.8 cm spigot nozzle was removed and tests were conducted with an effective spigot diameter of 1.6 cm. The test results indicated that the larger spigot had little effect on the ordinary cyclone (84% solids recovery), but the magnetic cyclone performance increased to 99% solids' recovery.

Using the larger spigot, tests were then undertaken with increased pulp density. Table 10.4 illustrates that the magnetic cyclone performance increases with increasing magnetite feed weight, and that at higher pulp

TABLE 10.3. Size Distribution Data for Tests 1 and 2 at 6 psi

Size (micron)	Test 1		Test 2	
	UF	OF	UF	OF
56	5.2	0	4.9	0
28	37.4	0	28.6	23.8
14	39.0	6.9	44.2	14.3
7	13.7	49.3	18.4	33.3
-7	4.7	43.8	5.9	28.6
	100.0	100.0	100.0	100.0

TABLE 10.4. Effect of Increased Feed Solids' Content on Solids' Recovery in the One Magnet Cyclone Configuration

Feed Solids(g)	UF Wt(g)	UF Wt%	OF Wt(g)	OF Wt%
500	15.1	99	0.2	1
1500	68.2	99	0.6	1
4000	210.3	100	0.6	0
5500	217.4	100	0.7	0

densities the solids' recovery figures approach 100%. An approximate calculation of the actual pulp densities used in these tests gives values of 1% to 10% solids by weight.

Table 10.4 shows that the magnetic cyclone is very effective at recovering magnetite in a range of feed densities, which is representative of the four plant process stream samples discussed later. However, the process stream samples gave quite different results, as discussed in the following section.

Test Results from Coal Plant Process Streams

Two Missouri coal mining operations, located in the Moberly district, were visited, and samples of two pulp streams at each mine were taken. At the first mine, the samples taken represented the tails (B) from the drum magnetic separator and the overflow product (A) from a cyclone, which concentrates the dilute magnetite pulps before it reaches the drum magnetic separator. Both samples represent streams, shown in Figure 10.6, in which magnetite could be lost. The first potential magnetite loss would result from magnetic separator inefficiency, and the second from magnetite fineness, which would keep the magnetite from being directed to the magnetic separators.

At the second mine, one sample was again taken from the drum magnetic separator tailing (M), but the other sample came from a final plant discharge slurry (S), containing the gangue or waste products. Table 10.5 provides physical data relating to the four samples. The data include magnetite content, solids concentration, and size parameters.

FIGURE 10.6. Sample Locations in Magnetite Recovery Circuit

TABLE 10.5. Physical Data for the Four Moberley Samples

Solids	Sample B	Sample A	Sample M	Sample S
Content (g/l)	111.5	46.2	182.7	125.0
Wt %	10	4	16	11
% Magnetite	4	96	100	0
% >150 microns	52	27	13	34
% <14 microns	16	39	39	20

Table 10.5 shows that samples A and M contain high proportions of magnetite, while sample S is surprisingly magnetite-free. The recovery of magnetite at the first mine is effective in the drum magnetic separators, but losses do occur in the cyclone overflow prior to magnetic separation. At the second mine, the magnetic separators are less effective and a tail containing virtually pure magnetite is produced.

The size distribution data are presented in Figure 10.7, which shows that the curves are not smooth, indicating that the samples are probably the combination of different materials. Because dense media magnetite is essentially less than 75 microns in size, the coarser material present in the samples most likely represents gangue materials from the raw coal. Samples A and M display a considerable proportion of particles less than 14 microns, representing a potential magnetite loss.

Sample A - Cyclone Overflow Product. The results of the tests using 500 g of solid from Sample A (96% magnetics) at a pressure of 6 psi are given in Table 10.6. The spigot diameter for all the four plant samples was maintained at 0.8 cm. These results show that the recovery of magnetite is very difficult even with the magnet configuration, which recovered only 33% of solids. This results from the extreme fineness of Sample A, which contains 39% of the particles finer than 14 microns.

FIGURE 10.7. Size Distribution Data for Plant Samples

TABLE 10.6. Circuit Configuration Effects on Solids' Recovery for Sample A

		Wt(g)	Wt% Recovery	Wt% Solids
5 No Magnet	UF	5.6	30	4.1
	OF	13.3	70	0.5
6 One Magnet	UF	5.6	33	4.2
	OF	11.2	67	0.5
7 Two Magnets	UF	5.4	32	4.1
	OF	11.3	68	0.5

Sample B - Magnetic Drum Separator Tail. The results from the circuit tests are given in Table 10.7 for the three configurations at 6 psi pressure drop for Sample B (4% magnetics). As expected from the analysis of the feed material, the magnetic recoveries are only slightly higher by using the magnetic cyclone because only 4% of the feed material is magnetite. Obviously, in this case it would be desirable to separate the magnetite from the gangue material by imposing conditions such that under normal cyclone conditions, all the material reports to the overflow. Then the application of a magnetic field would cause only the magnetite to report to the underflow. This could be achieved by using a larger diameter cyclone.

Sample S - Discharge Slurry. Because Sample S has no magnetic material, the magnetic cyclone test data are not relevant and are not reported here.

Sample M - Drum Magnetic Separator Tail. The results for the magnetic cyclone tests on Sample M (100% magnetics) are shown in Table 10.8. The table shows that the solids' recovery from Sample M, which contains essentially magnetite only, can be increased from 56% to 82% by applying a magnetic field across the cyclone. The size distributions of the cyclone products are shown in Figure 10.8, and it is apparent that the magnetic cyclone has recovered finer material to the underflow. Therefore, the overflow product has coarsened and the underflow product has become finer. Again, the fineness of the material (39% less than 14 microns) has made the recovery difficult.

10.3.3 Application 2 - Steel Plant Sludge Dewatering

The U.S. steel industry has encountered a severe problem with using and disposing of dry dusts or sludges resulting from steelmaking operations [Laboratory for Environmental Research (LER) 1988]. The various steel-making processes generate dusts as by-products, and these dusts are removed from furnace gases generally in wet scrubbers, which results in the production of sludges. About 10 to 20 kilograms of dust are generated per ton of liquid steel produced [U.S. Bureau of Mines (USBM) 1970]; this is equivalent to over 2 million tons of dust for a U.S. steel production rate of 130 million tons.

TABLE 10.7. Circuit Configuration Effects on Solids' Recovery for Sample B

		<u>Wt(g)</u>	<u>Wt% Recovery</u>	<u>Wt% Solids</u>
8				
No Magnet	UF	12.4	70	7.2
	OF	5.2	30	0.2
9				
One Magnet	UF	13.5	71	8.1
	OF	5.6	27	0.2
10				
Two Magnets	UF	13.4	72	7.7
	OF	5.2	28	0.2

TABLE 10.8. Circuit Configuration Effect on Solids' Recovery for Sample M

		<u>Wt(g)</u>	<u>Wt% Recovery</u>	<u>Wt% Solids</u>
11				
No Magnet	UF	11.2	56	8.7
	OF	8.7	44	0.4
12				
One Magnet	UF	13.2	62	9.9
	OF	8.0	38	0.3
13				
Two Magnets	UF	12.7	62	9.7
	OF	7.9	38	0.3

FIGURE 10.8. Size Distribution Data for Cyclone Products

These sludges contain appreciable quantities of iron (25% to 70%) and therefore represent an iron resource. Currently, this material is disposed of in landfills. As the presence of zinc in these sludges increases, the material becomes increasingly toxic and will dramatically increase future landfill costs. These sludges can be commercially recycled, but the recycling is limited to materials having a high zinc content because the recovered zinc values make the treatment process economical (Price 1986; Fossnacht 1985; Little 1983).

One major problem associated with treating all sludges is the removal of water to lower transport costs and to prepare the material for processing or efficient landfill disposal. A typical sludge contains from 5% to 30% solids by weight; for effective handling and treatment this must be raised to solids contents in excess of 70%. Steelmaking dusts typically are very fine (LER 1986), with median particles frequently ranging from about 8 to 10 microns. These sludges represent suitable feeds to small diameter cyclones, particularly if magnetic forces can be used to augment the normal classification forces.

Some sludges contain large proportions (up to 70%) of iron as magnetite, and it is the dewatering of these materials that represents a possible application for the magnetic cyclone. Because electric arc furnace (EAF) dusts are approximately 90% magnetic, they would be a good feed material for magnetic cyclone tests. Millscale also has a high iron content and is a suitable material for the magnetic cyclone. Table 10.9 summarizes the characteristics of these two potential feed materials for the magnetic cyclone.

At this time, no test work has been undertaken because samples from the steel industry were unavailable. Requests have been made to steel plants in the Northwest Indiana area, but to date no samples have been received. The test work will be undertaken when appropriate samples can be obtained.

TABLE 10.9. Characteristics of EAF and Millscale Material (LER 1986)

Material	%Fe	%Zn	100% Passing (microns)	Tons/Year
EAF	39-44	3-5	100	30,000
Millscale	72-78	3-5	500	726,000

10.4 FUTURE DEVELOPMENT

The first step needed to further develop this concept is to complete the initial assessment process. Then, the most promising application process for the magnetic cyclone can be identified. Other possible applications may arise and merit further investigations as a result of the project report and the oral presentation in Washington. Obviously, the primary requirement in any development plan is to interest a potential user, and then to construct a test rig on site and prove the concept on a pilot plant scale in a real industrial situation. The key to any utilization must be a process to permit the unique properties of the magnetic cyclone to be exploited.

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