To the Graduate Council :

I am submitting herewith a thesis written by Darryll Glen Rasnake entitled "Bench Scale Evaluation of the Solid-Liquid Separation Steps in the Formate Process Based Seed Reprocessing Option." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

Atul C. Sheth

Atul C. Sheth, Major Professor

We have read this thesis
and recommend its acceptance :

Accepted for the Council :

Vice Provost
and Dean of the Graduate School

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a Master's degree at The University of Tennessee, Knoxville, I agree that the Library shall make it available to borrowers under rules of the Library. Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgment of the source is made.

Permission for extensive quotation from or reproduction of this thesis may be granted by my major professor, or in his absence, by the Head of Interlibrary Services when, in the opinion of either, the proposed use of the material is for scholarly purposes. Any copying or use of the material in this thesis for financial gain shall not be allowed without my written permission.

Signature Daniel D. Rule

Date April 26, 1989

BENCH SCALE EVALUATION OF THE SOLID-LIQUID SEPARATION STEPS IN THE FORMATE PROCESS BASED SEED REPROCESSING OPTION

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Darryll Glen Rasnake

May 1989

Dedicated to my wife

Melanie Wright Rasnake

Without her constant guidance and support

this work would not have been possible

ACKNOWLEDGEMENTS

The author gratefully acknowledges the invaluable help and guidance from his major professor, Dr. Atul C. Sheth. Sincere appreciation is also given to Drs. Lloyd W. Crawford and James N. Chapman, for taking time to read and correct the manuscript. The experimental work was completed with the support and guidance of my work supervisor, Mr. Jeffrey K. Holt. Finally, sincere thanks are extended to Mr. Phillip Sherrill, Ms. Katherine Parks, Ms. Teresa Sloan, and Mrs. Birdie Farris of the UTSI Chemistry Laboratory for their assistance in the laboratory.

All work presented was supported by the United States Department of Energy under Contract number DE-AC22-87PC79671.

ABSTRACT

Coal-Fired Open-Cycle Magnetohydrodynamics (MHD) power generation system requires the use of a sulfur-free potassium salt as a seed material. This potassium seed when added to the coal before combustion serves the two-fold purpose of increasing plasma conductivity in the MHD channel and removing environmentally offensive sulfur compounds from the flue gas by forming K_2SO_4. Most of the seed material (over 85%) is collected in the form of potassium sulfate in the downstream particulate collection devices, with the remaining potassium being tied up as potassium aluminosilicates in the radiant furnace slag. Because of the high cost of fresh seed and limited commercial use of K_2SO_4, the disposal of spent seed is not economically feasible. Thus, a seed reprocessing scheme must be developed to collect and regenerate the spent seed.

In this work, the Formate Process-Based Seed Reprocessing Option is considered. A complete solid-liquid separation (SLS) system to recover the soluble potassium sulfate from spent seed is developed. Additionally, a SLS system to remove the insoluble gypsum formed in the Formate reactor is developed. Preliminary economics of the proposed solid-liquid separation system are completed and related to the overall cost of the Formate Process.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

A	Settler, centrifuge, or filter area, (cm^2)
$\bar{A}$	Unit area, (cm^2 s/g)
A_T	Total filter area, (cm^2)
C	Concentration of suspended solids, (g/cm^3)
C^*	Mass of solids per unit volume of filtrate, (g/cm^3)
d	Particle diameter, (cm)
d_t	Diameter of centrifuge tube, (cm)
f	Drum submergence of continuous filter, (dimensionless)
F_d	Drag force, (g cm/s^2)
F_g	Gravitational force, (g cm/s^2)
F_r	Radial force, (g cm/s^2)
g	Gravitational constant, (cm/s^2)
G	Solids mass flux, (g/cm^2 s)
H_u	Ultimate height, (ml)
K	Ratio of cylinder volume to height, (ml/cm)
n	Drum speed of continuous filter, (rad/s)
P_c	Difference in pressure across filter cake, (g/cm s^2)
P_m	Difference in pressure across the medium, (g/cm s^2)
P_T	Total pressure drop, (g/cm s^2)
Q	Volumetric flow rate, (cm^3/s)
r	Radius of axis of rotation, (cm)
r^*	True specific cake resistance, (cm/g)
r_o^*	Initial specific cake resistance, (cm/g)

r_{pc}^* Specific resistance of the precoat material, (cm/g)

R_c Cake resistance, (1/cm)

R_m Medium resistance, (1/cm)

R_T Total resistance, sum of R_c and R_m, (1/cm)

Re_p Reynolds number based on the particle diameter, (dimensionless)

s Cake compressibility factor, (dimensionless)

v Transport velocity, (cm/s)

v_s Settling velocity, (cm/s)

v_t Terminal velocity, (cm/s)

V Volume of centrifuge, (cm^3)

w Mass of dry suspended solids in cake per unit area, (g/cm^2)

W Mass of solids, (g)

Greek Letters

ζ Safety factor, (dimensionless)

θ Time, (s)

θ_a Time used in constructional procedures, (s)

θ_e Time used in constructional procedures, (s)

θ_g Time used in constructional procedures, (s)

θ_u Ultimate time, (s)

μ Viscosity of filtrate, (g/cm s)

π Numerical constant approximately equal to 3.14159, (dimensionless)

ρ_l Density of the liquid phase, (g/cm^3)

ρ_s Density of the solids, (g/cm^3)

Σ Equivalent area of centrifuge, (cm^2)

v Specific volume, (cm^3/cm^2)

ω Angular velocity, (cm/s)

Subscripts

a Denotes location 'a'

c Denotes critical

f Denotes feed

o Denotes overflow

u Denotes underflow

CHAPTER I

INTRODUCTION

MHD Background

Magnetohydrodynamics (MHD) power generation has the inherent advantages of increased efficiency and greater environmental acceptability when compared with conventional coal-fired power generation. In the MHD concept, the working fluid is obtained by combusting coal in a reducing atmosphere in the presence of an easily ionizeable species, such as potassium. The working fluid is then passed through a nozzle to impart a high velocity. In turn this fluid is passed through a magnetic field to generate electricity by Faraday's principle. The upstream portion of MHD technology is commonly referred to as the topping cycle. The partially combusted coal is then combusted to completion as in a conventional coal-fired power plant and electricity is produced from the traditional steam turbine and generator setup, also known as a steam bottoming cycle. A typical MHD power plant, as shown in Figure 1, would contain both the upstream topping cycle and the downstream steam bottoming cycle.

As part of the continuing national program on MHD technology development, the University of Tennessee Space Institute (UTSI) is currently under contract with the Department of Energy (DOE) to provide testing in a 28 MW_t low mass flow (LMF) facility. The major objective of the UTSI work is to provide testing and evaluation of downstream components. As part of this objective, UTSI is also involved in determining the disposition of potassium containing species in the downstream equipment.

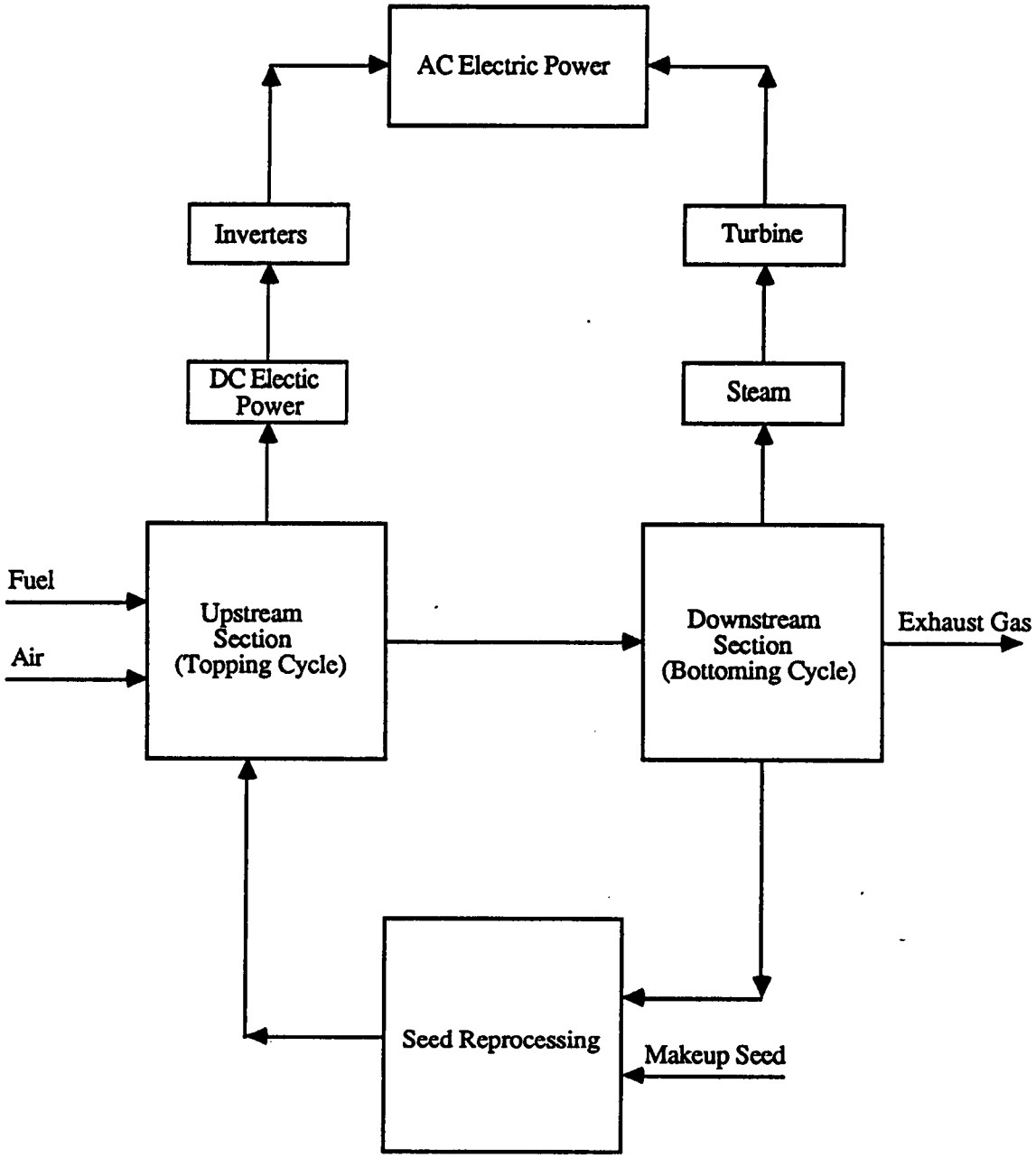

Figure 1. Typical MHD Power Plant

The Coal Fired Flow Facility at UTSI

At the MHD Coal Fired Flow Facility (CFFF) located in Tullahoma, Tennessee, as shown in Figure 2, K_2CO_3 seed material is mixed with pulverized coal. The seeded coal is then fed to the combustor where it is combusted in a reducing atmosphere to create a plasma containing 1 percent by weight potassium. The plasma is then fed through a nozzle to impart a high velocity. As the plasma passes through the channel section, direct current would be produced by Faraday's principle if an MHD generator were present. This current would be extracted by means of a system of electrodes located along the channel. Current tests in the CFFF are being conducted with a dummy duct in place of the MHD generator since the primary objective of the UTSI work is to study downstream components.

The partially combusted gases exit the diffuser section and enter the downstream section of the furnace and secondary combustor system. At this point some of the potassium is tied up with the oxides of aluminum and silicon as insoluble aluminosilicates and is removed with the radiant furnace slag. Further downstream in the secondary combustor, the combustion of the hot gases is completed. The combustion products then pass through heat recovery devices where steam is produced for further power generation. In these downstream components the potassium combines with the sulfur containing combustion products to form K_2SO_4. This material is deposited in small amounts on the heat exchanger tubes found in the air heater and the superheater test modules. The majority of the spent material along with flyash from the coal is carried downstream to the particulate control devices, i.e. the baghouse (BH) and electrostatic precipitator (ESP). At this point, the particulate is collected and stored for future separation and reprocessing of the seed material.

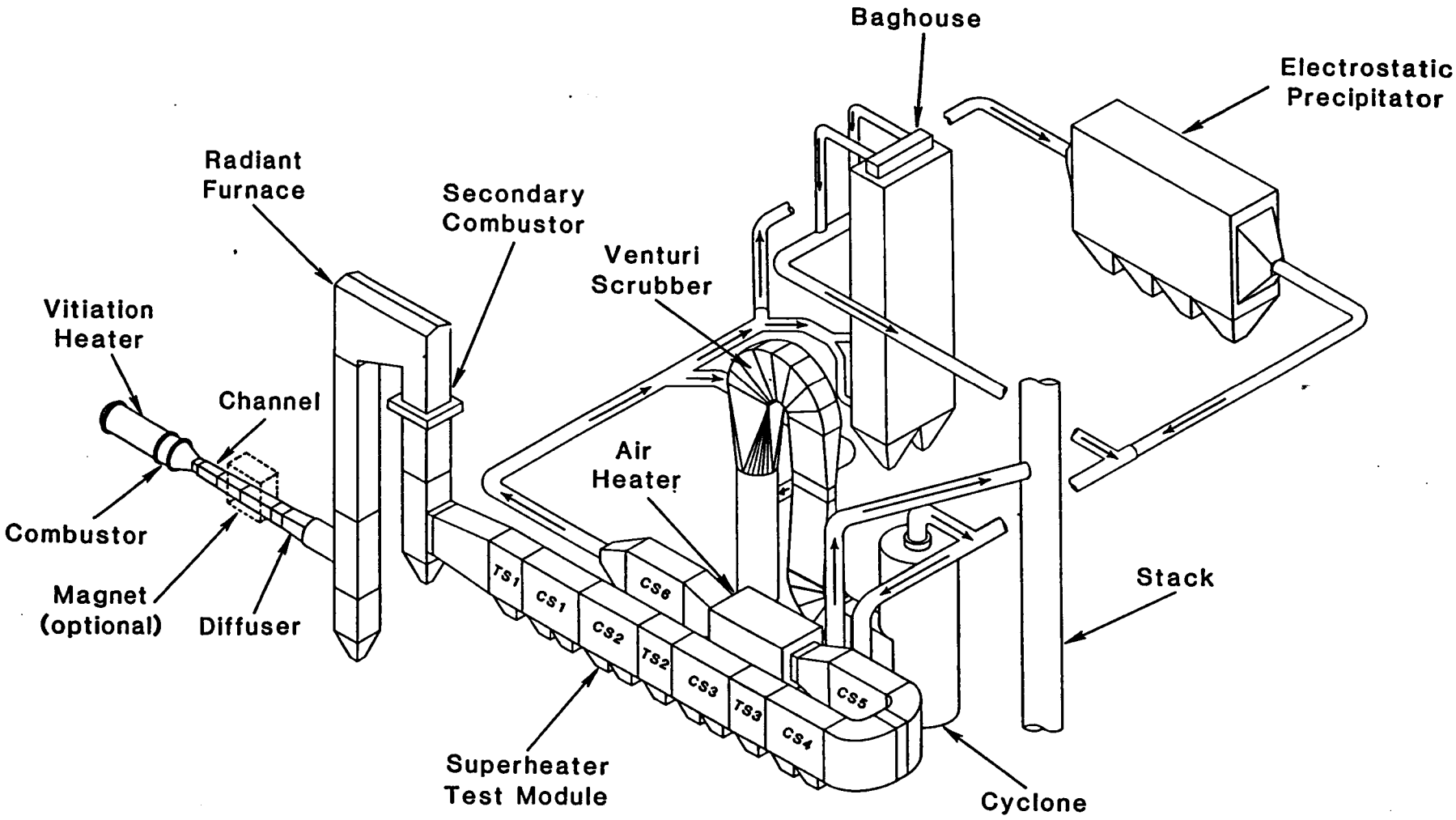

Figure 2. Coal-Fired Low Mass Flow Facility at UTSI

Seed Reprocessing

In addition to having a higher efficiency, the MHD system has a built in means of SO_2 removal. In particular the potassium seed material, if introduced in sulfur-free forms such as K_2CO_3 or KCOOH, will remove the sulfur from the effluent gas stream in the form of K_2SO_4. The seed material therefore serves a dual purpose: (1) it provides the necessary ionic species to increase conductivity in the topping cycle, and (2) it removes the environmentally offensive sulfur containing compounds in the steam bottoming cycle.

Because of the large difference in cost of the seed material from sulfur-free forms to sulfur-rich forms, a once-through throw-away system which produces spent seed as K_2SO_4 is not economically feasible. The spent seed material is also highly soluble, containing more than 85 percent by weight K_2SO_4, and therefore would be difficult to dispose of in any satisfactory manner. Because of these reasons, there is a strong incentive to develop a process to regenerate (or desulfurize) the seed material into a sulfur-free form.

Seed Reprocessing Options

Seed reprocessing involves the recovery, regeneration, and recycle of spent seed material. The majority of the seed material (greater than 85 percent) which must be reprocessed is in the form of potassium sulfate. This potassium must be separated from the flyash material collected in the particulate control devices. A small portion of the potassium must also be recovered from the insoluble slag material.

Seed reprocessing options generally fall into one of three categories [1]. They are: (1) processes involving a reduction of K_2SO_4 to K_2S or K_2S_2, typified by the

Modified Tampella, Aqueous Carbonate, Carbon Reduction, and PERC Processes, (2) electrochemical processes, including the Electrodialysis Process, and (3) precipitation processes in which calcium sulfate (gypsum) is produced, represented by the Econoseed, Engel-Precht, Formate, and Hydrated Lime Processes. Currently under study through contract with the DOE's Pittsburgh Energy Technology Center (PETC) are three of these options: (1) the Formate Process, being studied by UTSI, (2) the Modified Tampella Process, being studied by Babcock and Wilcox Company, and (3) the Econoseed Process, being studied by TRW, Inc. As part of this contract effort, the team of UTSI and Resources Conservation Co. (RCC) has developed bench scale data on the Formate Process. The Formate Process uses a reducing gas (CO) and strong base ($Ca(OH_2)$) to convert the potassium sulfate into the sulfur-free potassium formate by the following reaction [2]:

$$K_2SO_4 + Ca(OH)_2 + 2CO \xrightarrow{473K, P_{CO}=30atm} 2KCOOH + CaSO_4 \qquad (1)$$

If necessary, the potassium formate can be further oxidized to form potassium carbonate as:

$$2KCOOH + O_2 \xrightarrow{673K} K_2CO_3 + H_2O + CO_2 \qquad (2)$$

The Formate Process

Figure 3 gives a block diagram of the Formate Process-based MHD seed reprocessing option that is proposed by the team of UTSI and RCC. Under this proposed processing scheme, spent seed material would be introduced with water as a solvent into a dissolution tank maintained at elevated temperature. Separation of the insolubles (composing approximately 15 percent by weight of the spent seed) would take place in some type of clarifier device, followed by either filtration, or centrifugal separation to further dewater the sludge. Based on prior work

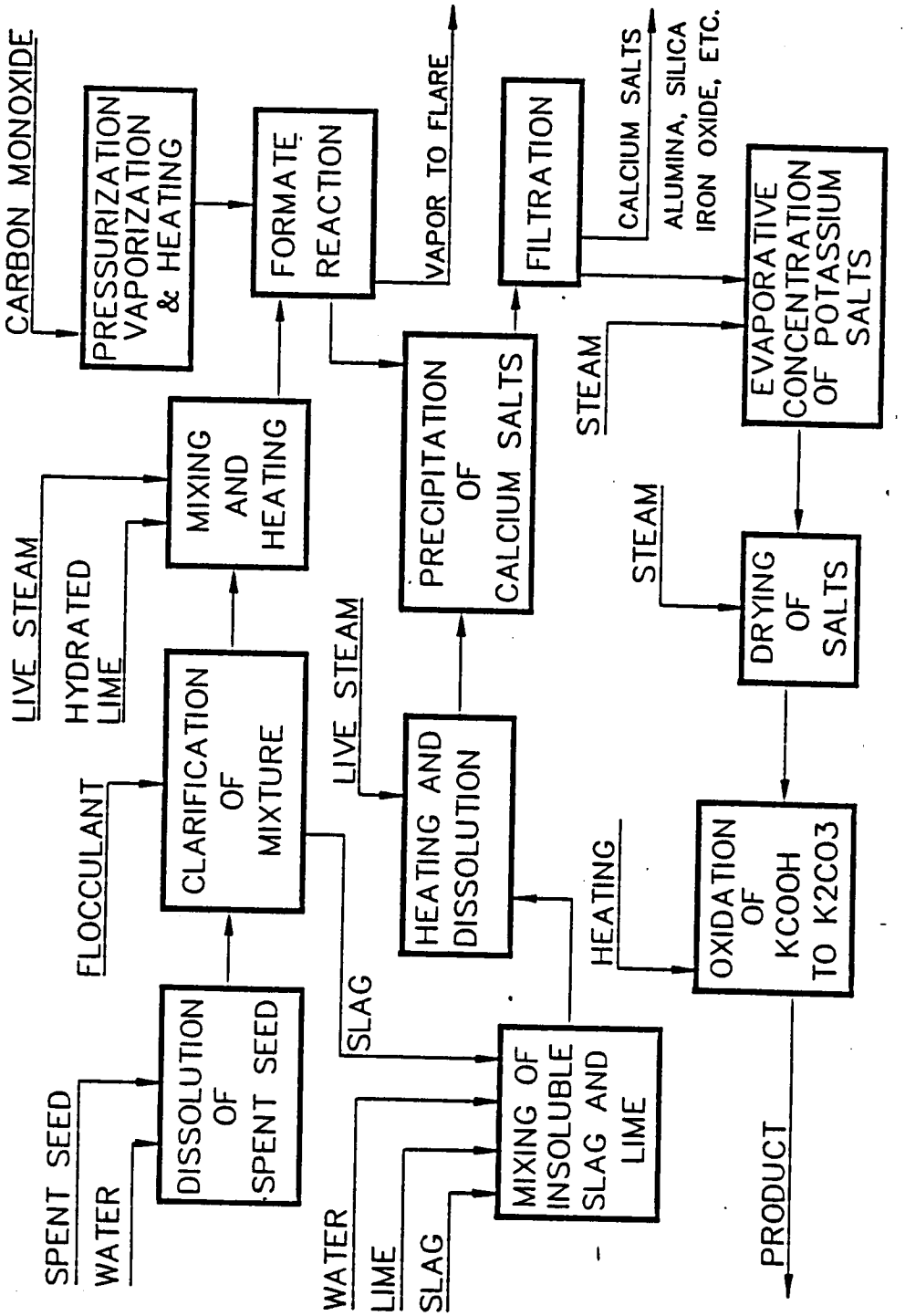

Figure 3. The Formate Process [2]

done on solid-liquid separation (SLS) of the spent seed slurry, filtration without pre-clarification has proven to be inadequate. Hence, other methods or combination of methods of solid-liquid separation need to be studied in order to determine the best means to perform this important step in the Formate Process-based seed reprocessing option. The clear liquid (overflow) from the clarifier is mixed with lime and fed to the formate reactor. After dewatering, the insoluble slag-like material is mixed with radiant furnace slag and leached at elevated temperature in the presence of a strong base, in this case $Ca(OH)_2$. The resulting product stream is combined with the formate reactor product stream. Filtration of the resulting product mixture to remove the insoluble calcium sulfate will also be studied to determine the best conditions for further processing of the formate containing solution.

Objectives

The main objective of this study is to use bench scale data collected during the Phase I contract effort at UTSI on the Formate-based seed reprocessing option to develop and design a solid-liquid separation system for the Formate Process. Solid-liquid separations will be required in the following areas: (1) separation of the insoluble flyash material from the potassium sulfate containing liquid fraction, and (2) separation by filtration of the insoluble calcium sulfate from the soluble product stream containing potassium formate.

For the separation of the insoluble flyash material, several options will be considered including the use of a clarifier, filter, or centrifuge, or some combination of these items. Design calculation will be made based on experimental data to determine the size and best configuration of these items.

For the separation of the formate containing product stream from insoluble

calcium sulfate, a filter will be used as the base configuration. Design parameters of this piece of equipment will be calculated based on the experimental data. The need for a wash cycle to recover additional soluble potassium and the parameters of this cycle will also be determined.

Approach

The proposed study involves a significant amount of both experimental and theoretical work. Based on the experimental results, theoretical calculations of various design parameters will be completed and compared with literature. Optional configurations of the solid-liquid separation hardware for the Formate Process-based seed reprocessing concept will be developed and designed. Based on these results, the optimum configuration will be determined. A preliminary cost estimate will be made to determine the economic feasibility of the selected configuration and its impact on the overall economics of the Formate Process-based seed reprocessing option.

CHAPTER II

LITERATURE SURVEY

Prior Work on Slag and Spent Seed Insolubles

The potassium aluminosilicates found in slag and spent seed insolubles can be chemically decomposed in the presence of either strong acids or strong bases. Exxon Corporation [3] reports that these silicates can be reacted with lime at elevated temperatures to give potassium hydroxide:

$$2KAlSiO_4 + 3Ca(OH)_2 + 2H_2O \xrightarrow{420K} Ca_3Al_2SiO_4(OH)_8 + SiO_2 + 2KOH \quad (3)$$

and

$$4KAlSiO_4 + 11Ca(OH)_2 + 4SiO_2 + 4H_2O \xrightarrow{420K} 4KOH + 2Ca_3Al_2SiO_4(OH)_8 + (CaO)_5(SiO_2)_6(H_2O)_5 \quad (4)$$

Strong acid solutions can also leach significant amounts of potassium at room temperature. Based on previous work by Holt [4] at the UTSI, the extractant compositions which can be expected in an acid extraction and a base extraction differ greatly. Most notably, acid extraction will leach cations other than potassium equally well. Holt reports that more than 80 percent of the iron,titanium, and sodium will be leached as impurities in the presence of a 1N sulfuric acid at 25 °C. Additionally, silicon will be leached in amounts approaching 100 percent under the same conditions. The only major impurity found in base extraction was aluminum which Holt suggests can be removed by fractional crystallization if necessary. Also evident from the study at UTSI is the fact that the extractant obtained from acid

extraction will only contain approximately 30 percent potassium by weight in the dissolved solids with the remainder being impurities. In contrast, the extractant from lime digestion will contain almost 90 percent potassium hydroxide by weight in the dissolved solids. Strong acids also pose a corrosion problem for system hardware. In addition to this, the acid solutions will require neutralization before processing can continue. Thus, it turns into a two-step process involving acid extraction followed by neutralization with a suitable base. Furthermore, the potassium obtained by acid extraction by sulfuric acid will not be sulfur-free, requiring further processing to be regenerated. On the other hand, base extraction with lime requires only one step to give potassium in a sulfur-free form. Because the Formate Process uses calcium hydroxide, base extraction is especially attractive. Resources Conservation Co. [5] reports that the potassium hydroxide formed and any excess lime left over from the digestion step will aid the process by keeping the pH high ($\geq$10) thus preventing the formation of formic acid and the resulting corrosion of downstream components. Because of the overwhelming advantages offered by the base extraction method, the Formate Process uses base extraction to recover potassium from slag and spent seed insolubles.

Due to the extensive amount of work already completed on slag leaching, the only area of interest will be the effect of the slag leachate from base extraction on the filtration characteristics of the formate reactor products. To accomplish this, the leachate from base extraction will be mixed with the formate reactor products in an amount representative of the amount likely to be found in a full-scale plant. This slurry will then be filtered to determine the filterability of the mixture.

Prior Work on Spent Seed

A single test run on the solubility of spent seed in water was examined by Templemeyer *et al* [6]. The results of this study did indicate that more than 95 percent of the potassium contained in MHD spent seed could be recovered by water extraction.

A more extensive study was completed by Patil [7] on the dissolution of spent seed material. Patil studied the effect of process variables such as particle size, temperature, concentration (i.e. solid-liquid ratio), and solid-liquid contacting time on spent seed dissolution. His results indicated that almost 100 percent of the soluble potassium was recovered from spent seed at room temperature in short mixing time (less than 15 minutes). Additionally, the most effective solution-to-solid ratio was found to be 10:1. Patil also incorporated experimental work done on the extraction of potassium from slag and spent seed insolubles by previous investigators to define a complete spent seed recovery system.

The lack of information on spent seed reprocessing now lies in the area of solid-liquid separation. In particular, Patil did not study the methodology required to actually separate the insolubles contained in spent seed from the soluble fraction. Additionally, for the proposed Formate Process, experimental data must be collected and evaluated in the area of efficient separation of the insoluble gypsum from the product stream containing potassium formate and potassium hydroxide and complete recovery of the soluble potassium from the filter cake by a suitable cake washing cycle.

CHAPTER III

THEORETICAL BACKGROUND

Theory of Continuous Zone Settling

Particles heavier than the suspending liquid can be removed from that liquid by mere settling, in which the fluid velocity is low and the particles possess a large settling velocity or can be made to have such by agglomeration, or flocculation of the solids. Settling, or thickening, is characterized by the sedimentation behavior commonly known as line settling. Solids subside with a clear line of demarcation between the settling solids and the clear supernatant. The condition required for line settling is that all of the particles must have the same subsidence rate, so that they settle at the same rate. This can exist under two circumstances: (1) The particles are all of the same size and therefore have the same settling rate; this can be simulated by a mixture which is characterized by a small standard deviation about some mean, or (2) The particles are flocculated such that they exist as uniform particle groups; this also can be true if the flocculant fibers are interlaced to cause the smaller, unflocculated particles to be towed along with larger flocculated groups. If the floccules are separate such that they do not interact with one another, they are said to be undergoing free settling. As the underflow material becomes more concentrated, the floccules interact and transmit compression stress. This zone is therefore called the compression zone.

Coe and Clevenger assumed that during "free settling"the settling rate v_s could be written as a function of concentration, i.e. $v_s = v_s(C)$, where C is the concentration of the suspended solids [8]. For steady state operation of a continuous thickening system, the downward velocity of the solids can be given as

the sum of two components: (1) the settling velocity v_s of the solids with respect to the suspension, and (2) the transport velocity v_u of the suspension resulting from the underflow withdrawal (the subscript u referring to the underflow phase). Therefore:

$$G = C(v_s + v_u) \tag{5}$$

The mass flux of the system G must also be given by the boundary condition:

$$G = C_u Q_u / A \tag{6}$$

where C_u is the concentration of the solids in the underflow and Q_u is the flow rate of the underflow material leaving the settler. Equating and noting that v_u can be written as $v_u = Q_u/A$, where A is the area of the settling pool, the mass flux is therefore given as:

$$G = C(v_s + \frac{Q_u}{A}) = \frac{C_u Q_u}{A} \tag{7}$$

Eliminating the term Q_u/A, equation 7 can be rewritten as:

$$G = \frac{v_s}{1/C - 1/C_u} \tag{8}$$

This equation is the original representation of the Coe-Clevenger model.

If v_s is only a function of concentration C then batch tests can be used to model a continuous system. Using this characteristic, a set of fluxes can be determined from experimental data and plotted versus concentration. A representative plot is given in Figure 4. The important empirical fact shown in Figure 4 is that there is usually a minimum in the plot of G versus C at some critical concentration C_c. If the feed concentration C_f is lower than C_c (as is often the case) and the underflow concentration C_u is higher, then the maximum solids flux which can pass to the underflow is given by G_c. Therefore, G_c defines the upper limit on solid

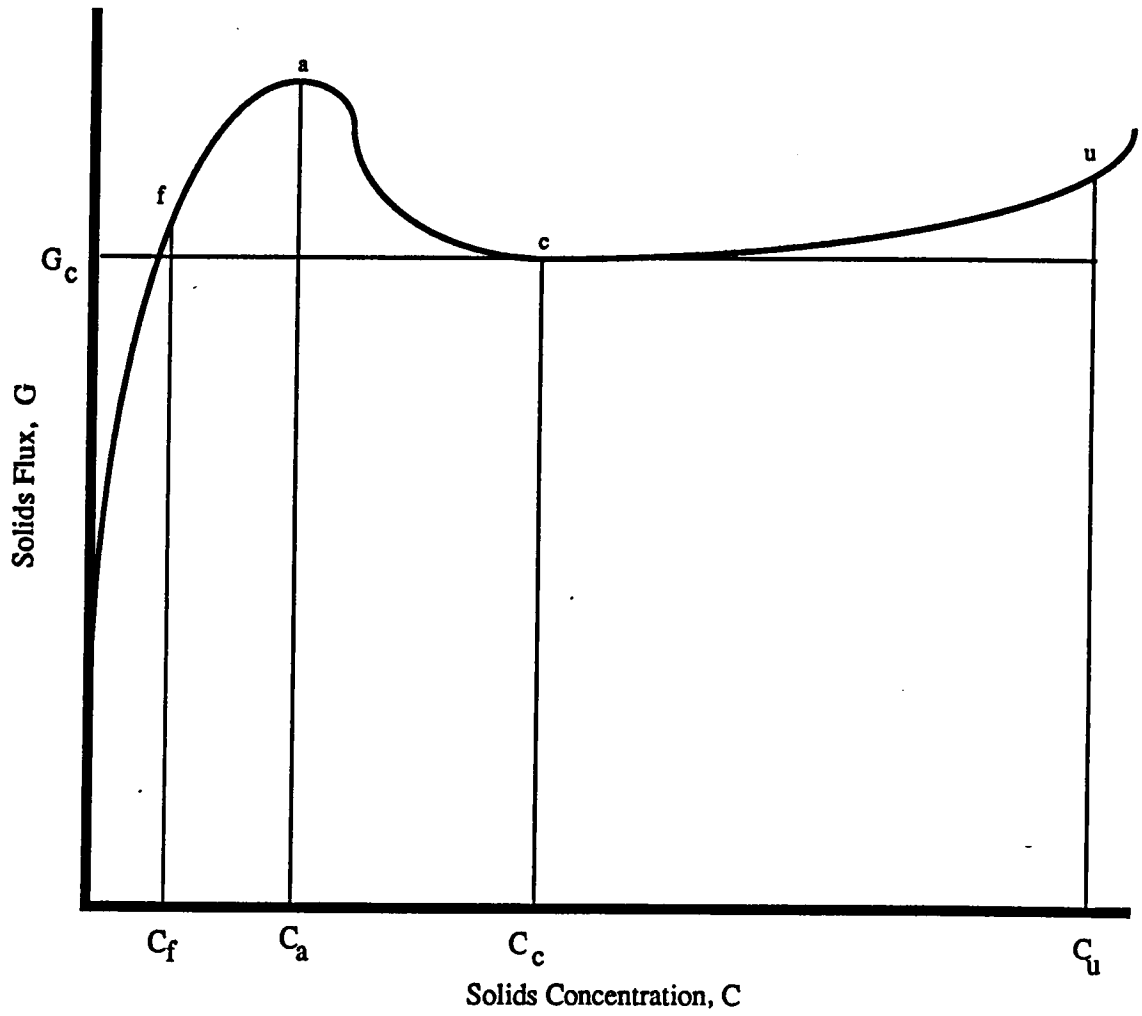

Figure 4. Solids Flux Versus Solids Concentration

flux. If the solids loading is greater than this, a critical zone of concentration C_c will be created. Solids cannot pass through this zone as fast as they are supplied; therefore, the size of the zone increases until it fills the clarifier and solids enter the overflow. If solids in the overflow solution are unacceptable, the area of the thickener must be sufficient such that the solids flux does not exceed the critical value. Thus the condition is specified to impose an area demand on the thickener design.

If on the other hand $G_f < G_c$, then solids pass through the zone faster than they are being replenished. The zone therefore gets smaller and eventually will disappear.

Theory of Cake Filtration

The flow of liquid through a compressible filter cake supported on a filter medium (Figure 5) can be represented based on Darcy's Law for flow through a porous media and given by the equation [9]:

$$\frac{dv}{d\theta} = \frac{P_T}{\mu} \cdot \frac{1}{(R_c + R_m)} \tag{9}$$

where v is the cumulative volume of filtrate collected per unit area over time θ. P_T is the total pressure drop with μ being the filtrate viscosity. R_c and R_m are the cake and medium resistances, respectively. Note that since the cake resistance is constantly increasing as the solids build up on the media, the cake resistance can be expressed as a function of the weight of solids accumulated, where w is the mass of dry solids in the cake per unit area of surface, and equation 9 becomes:

$$\frac{dv}{d\theta} = \frac{P_T}{\mu} \cdot \frac{1}{(r^* w + R_m)} \tag{10}$$

where r^* is the specific resistance of the cake. Now by assuming that the medium resistance is small ($R_m \rightarrow 0$) in comparison to the cake resistance, in terms of

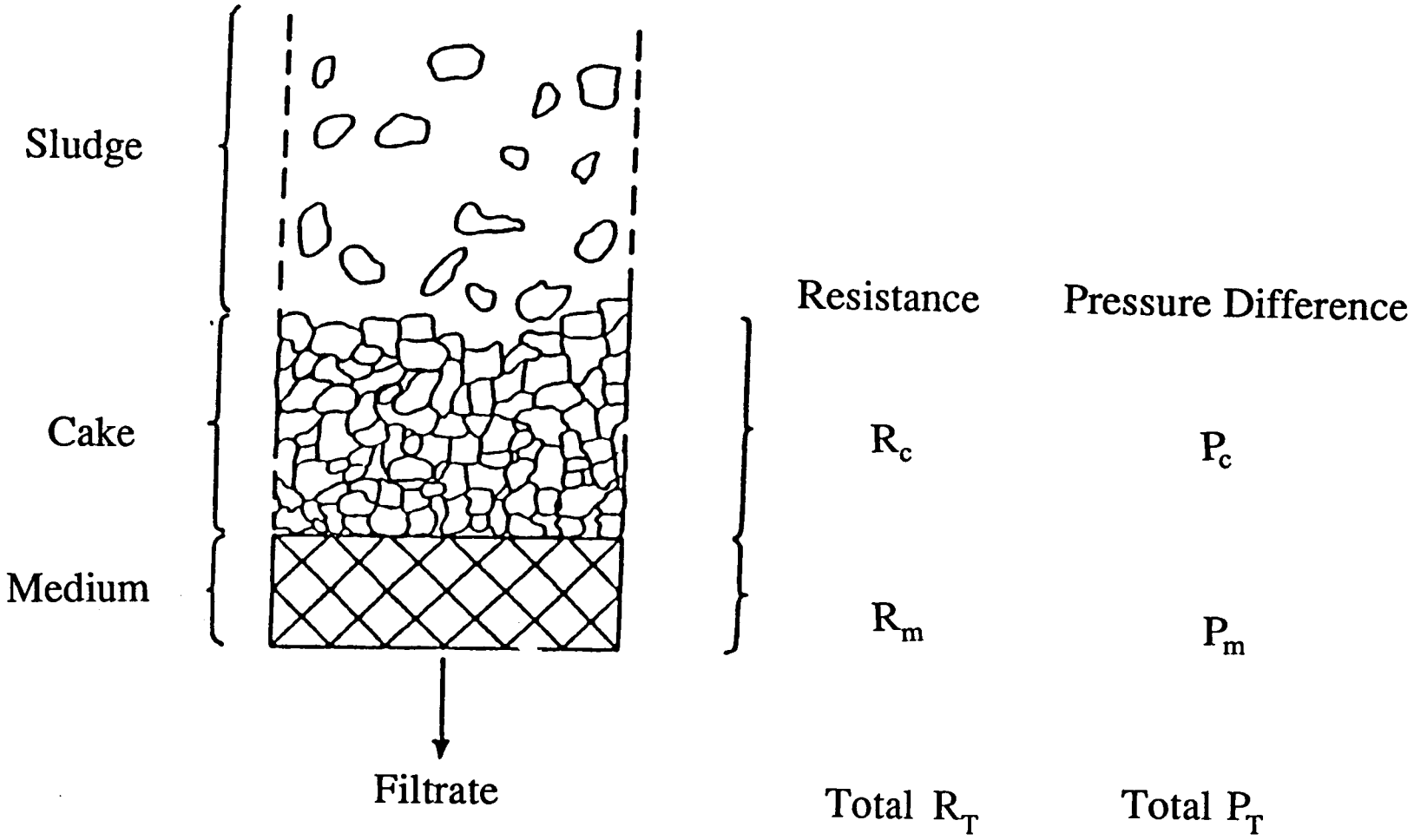

Figure 5. Physical System for Separation by Filtration

specific resistance equation 10 can be written as:

$$r^* = P_T\left[\frac{1}{\mu w} \cdot \frac{1}{(dv/d\theta)}\right] \tag{11}$$

The specific resistance therefore is the pressure drop required to produce a unit rate of flow through a cake having unit weight of solids per unit area. Thus for any values of μ and w, the higher the pressure drop the higher the specific resistance, as expected.

The specific resistance can be related to pressure drop as proposed by Lewis [10] as:

$$r^* = r_o^* P_T^s \tag{12}$$

where s is the compressibility factor. A value for s of zero implies that the cake is incompressible with compressible cakes having values for s ranging from 0.2 to 0.8. r_o^* is the specific resistance of the cake to filtration at unit differential pressure (pressure drop).

For incompressible cakes, equation 9 must be integrated with R_m taken to be constant to give:

$$\frac{\theta}{v} = \left(\frac{\mu r^* w}{2P_T}\right) + \frac{\mu R_m}{P_T} \tag{13}$$

If w is considered to be a function of v, as $w = C^* v$, where C^* is the mass of suspended solids per unit volume of filtrate collected, equation 13 is:

$$\frac{\theta}{v} = \left(\frac{\mu r^* C^*}{2P_T}\right) v + \frac{\mu R_m}{P_T} \tag{14}$$

As can easily be seen, the slope of the plot of θ/v versus v yields the cake resistance while the intercept gives the medium resistance.

Theory of Centrifugal Separation

The use of centrifugal force for sedimentation of particles from a suspending fluid utilizing the difference in density between the two has been developed theoretically by other researchers [11],[12]. Whenever a force is applied to a particle, the particles accelerates to its terminal velocity (Figure 6). For a spherical particle of diameter d, this radial force also known as the rotational force is given by:

$$F_r = \frac{\pi}{6} d^3 (\rho_s - \rho_l) \omega^2 r \tag{15}$$

where ρ_s and ρ_l are the solid and liquid densities, respectively. The angular velocity ω and arm radius r are characteristic of the centrifuge. The force opposing sedimentation, known as the drag force, is given by Stokes Law as:

$$F_d = 3\pi\mu d\, v_s \tag{16}$$

Also acting on the system is the force of gravity, F_g. In the case of the centrifuge, the gravitational force is small when compared to the rotational and drag forces (i.e. F_g is taken to be zero). Therefore, at equilibrium $F_r = F_d$ and the settling velocity, v_s, is given by the equation:

$$v_s = \frac{(\rho_s - \rho_l) d^2 \omega^2 r}{18\mu} \tag{17}$$

This does assume that the Reynolds number of the particles, given as $Re_p = d\rho_l v_s/\mu$, is less than 0.2, a good assumption for very small particles of average density. Since v_t, the terminal velocity, is given by Stokes Law as:

$$v_t = \frac{(\rho_s - \rho_l) g d^2}{18\mu} \tag{18}$$

the settling velocity, v_s, is a function of the terminal velocity the particle would reach in a gravitational field and the centrifugal force applied by the relation:

$$v_s = v_t \frac{r\omega^2}{g} \tag{19}$$

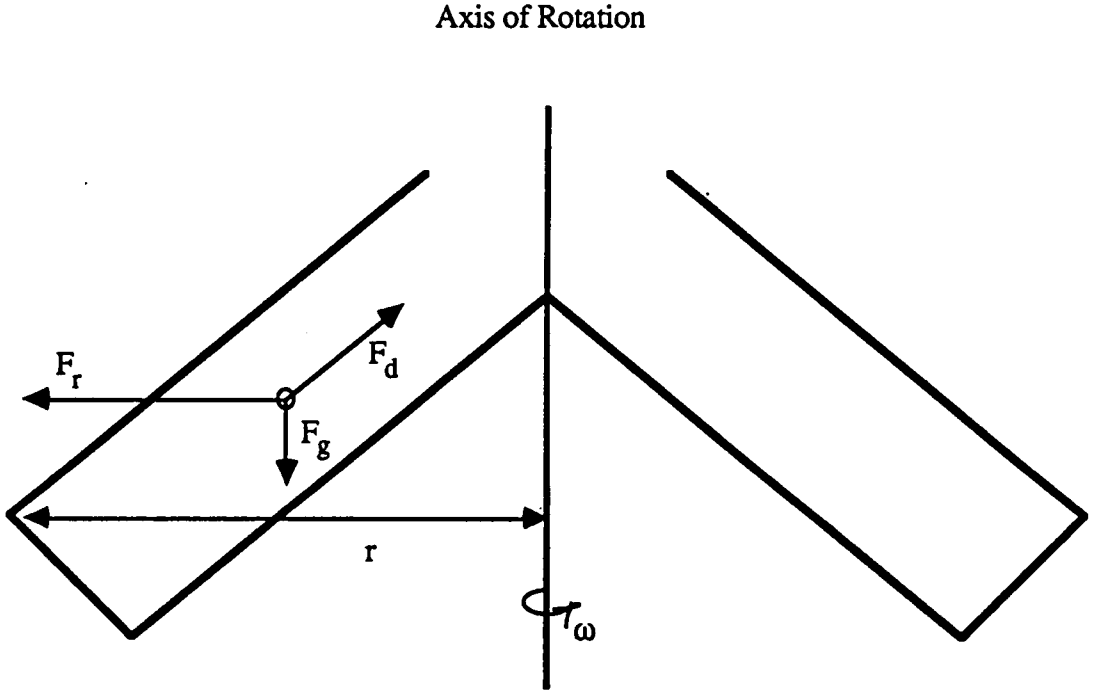

Figure 6. Force Diagram for Tubular Centrifuge

Note that although the term g appears in both of the previous equations, the gravitational term does not enter into the calculations and is included only so that the settling velocity can be written in terms of a well-understood parameter, the terminal velocity, v_t. If we assume that the time to accelerate to the settling velocity is very small (on the order of 1.4 x 10^{-2} sec for a 100 μm sized particle with density of 3 g/cc) and the thickness of the liquid layer is $d_t/2$, the settling velocity v_s can also be written as:

$$v_s = \frac{d_t}{2\theta} \tag{20}$$

where θ is the residence time in the centrifuge, given by:

$$\theta = \frac{V}{Q} \tag{21}$$

V is the volume of the centrifuge, while Q is the volumetric flow rate through the system. Combining equations 19 and 20 and solving for Q gives:

$$Q = \frac{2Vv_s}{d_t} = \frac{2Vv_t r\omega^2}{gd_t} \tag{22}$$

CHAPTER IV

DESIGN CONSIDERATIONS

Characterization of Settler Area

A typical plot of interface height (the boundary between relatively clear liquid and the concentrated sludge) versus time is shown in Figure 7. During the early stage of settling the velocity is constant, as shown by the first portion of the curve denoted as the constant rate section. This regime consists of unhindered settling of the particles in a clarifier type zone. As solids accumulate in the compression zone, the rate of settling decreases and steadily drops until the ultimate height is reached. This hindered settling, or thickening, involves concentration and compression of the solids. The critical point (point c) is reached when the compression of the solids begins (also known as the compression point). Calculation of the critical point and the corresponding critical time can be made based on a number of methods including the Oltmann and Talmadge-Fitch constructions. Using these semi-empirical methods, various design parameters for the clarifier/thickener can be determined and compared.

The determination of the critical point is based on the Coe-Clevenger model. On the basis of this model the compression point is the point at which the suspension below the interface of clear liquid and concentrated sludge changes from a zone of settling into compression. This is commonly taken to be the second point of discontinuity. Often it is difficult to determine the exact location of this second discontinuity. In such cases a log-log plot may be applied to make the discontinuities more apparent as shown in Figure 8. Another method used in the past for determining the critical point is the bisection method [13]. As given in Figure 9, a straight line is constructed along the linear portion of the settling curve and

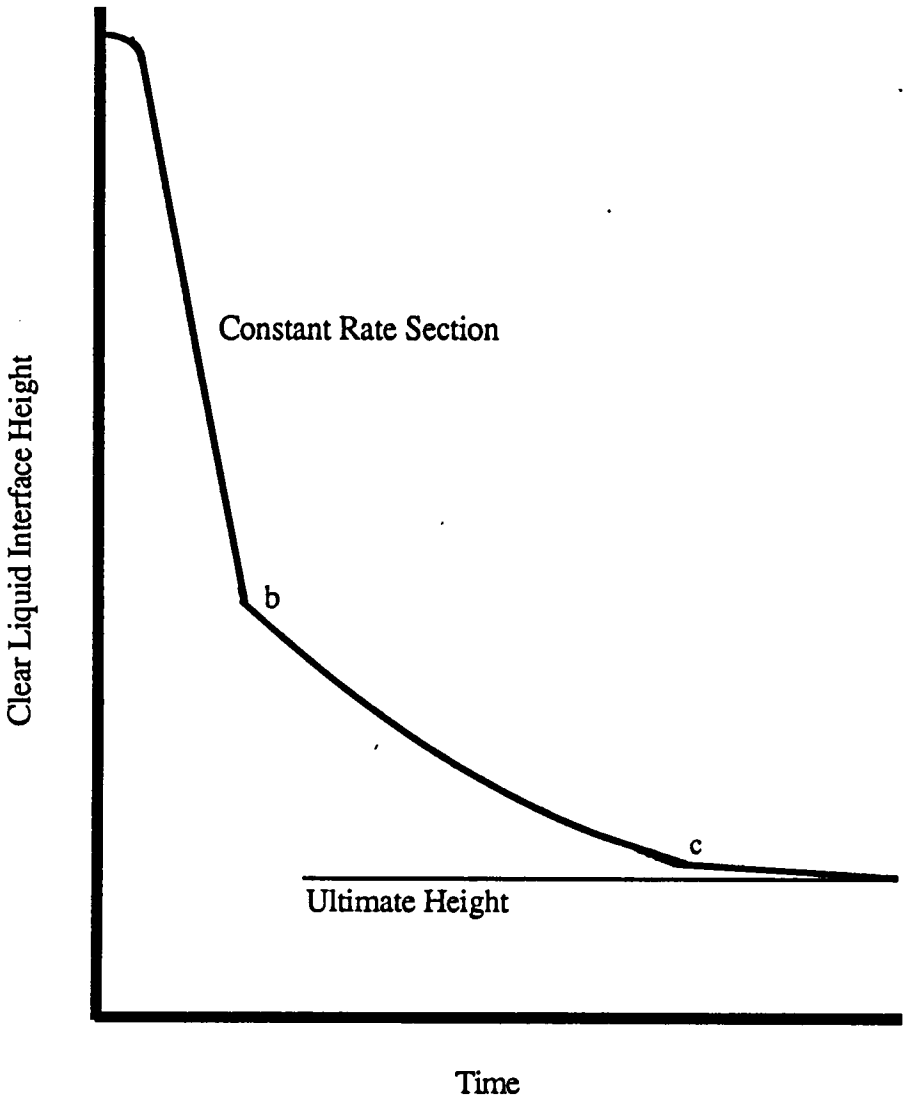

Figure 7. A Representative Plot of Clear Liquid Interface Versus Time

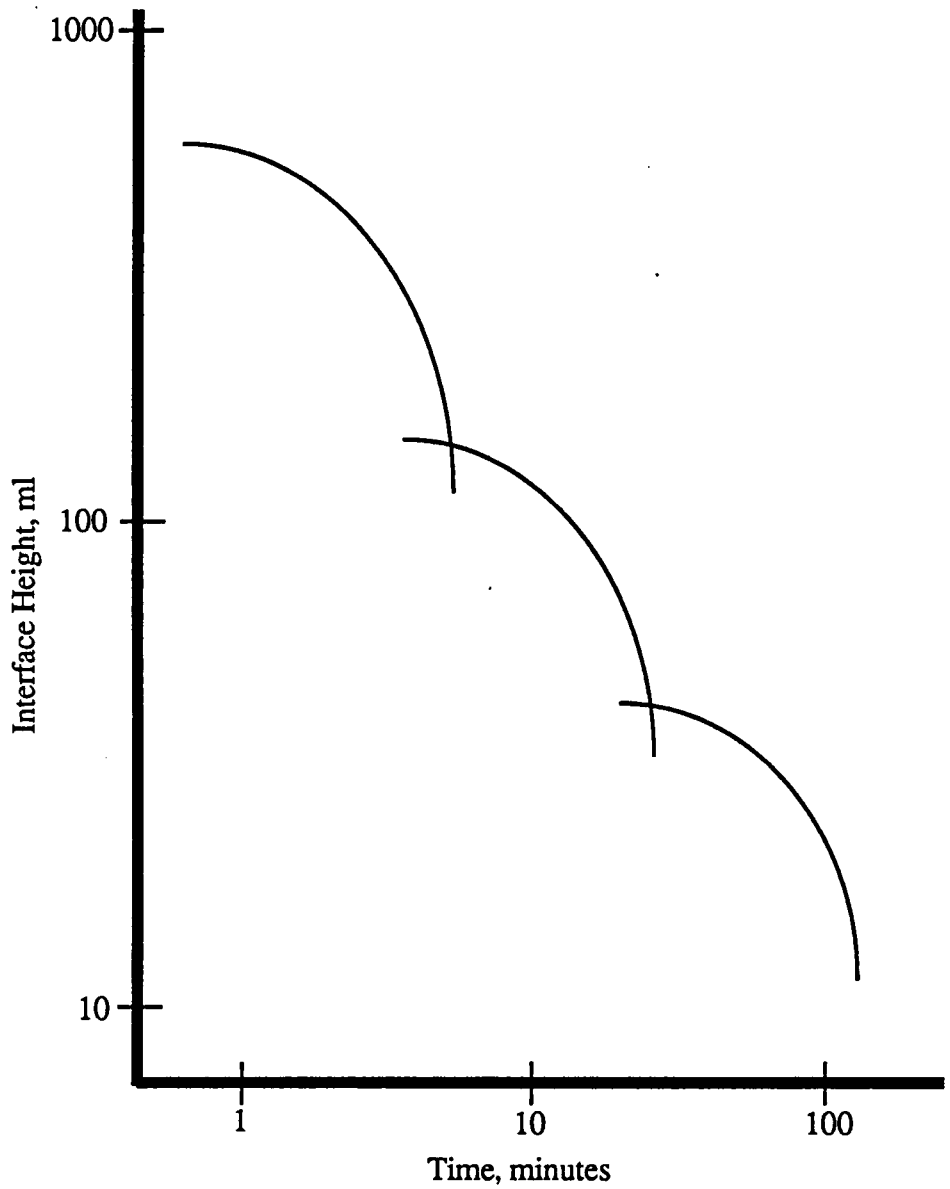

Figure 8. Determination of Critical Point by Log-log Plot Method

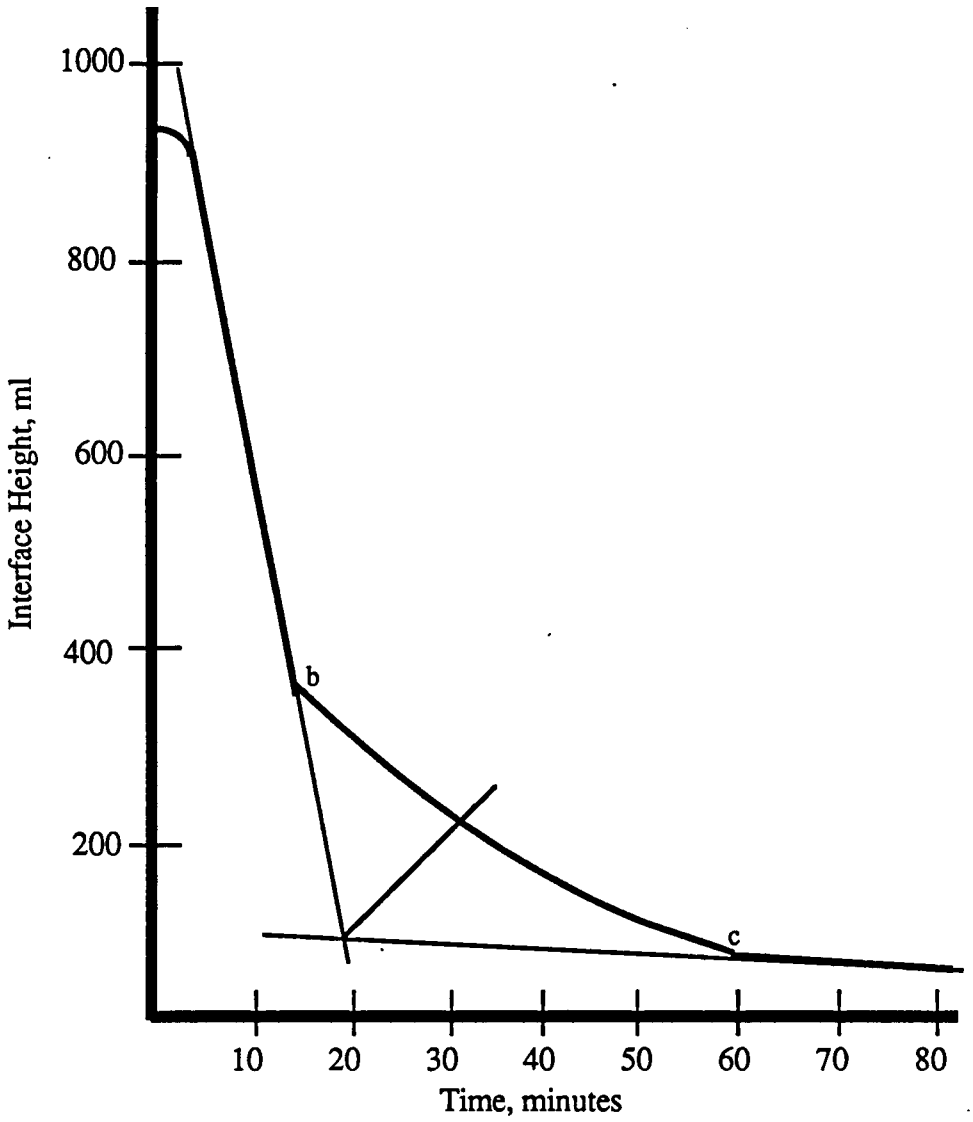

Figure 9. Determination of Critical Point by Bisector Method [13]

another straight line is drawn along the high time portion of the settling curve. The angle formed by these lines is bisected. The intersection of the bisector and the settling curve is the critical point.

A representative Oltmann construction is given in Figure 10 [8]. After determination of the critical point by one of the methods given above, a line is drawn from the first point of inflection (point a) through the critical point c to intersect a line representing the ultimate interface height at infinite time. This intersection of lines defines θ_e. The ultimate time is given by the equation:

$$\theta_u = \theta_e - \theta_a \tag{23}$$

The corresponding critical thickener flux G_c is then:

$$G_c = \frac{W}{\zeta K \theta_u} \tag{24}$$

where W is the weight of solids used in the cylinder test and ζ is a dimensionless safety factor representing an overdesign of the equipment. The safety factor generally ranges from 1 to 3. K is an expression which relates the geometric dimensions of the cylinder used in the settling test, i.e. the ratio of volume to height.

The Talmadge-Fitch method is identical to the Oltmann method except in the calculation of θ_u. A tangent is drawn at the critical point (given by line fg). Its intersection with the underflow line gives θ_g. As in the Oltmann procedure, $\theta_u = \theta_g - \theta_a$.

Results can be reported as unit area, which is the reciprocal of solid flux given by:

$$\bar{A} = 1/G_c \tag{25}$$

where $\bar{A}$ is given as the area per unit weight per time. Thus it represents the settler area required to treat a certain amount of solids material in a given time period.

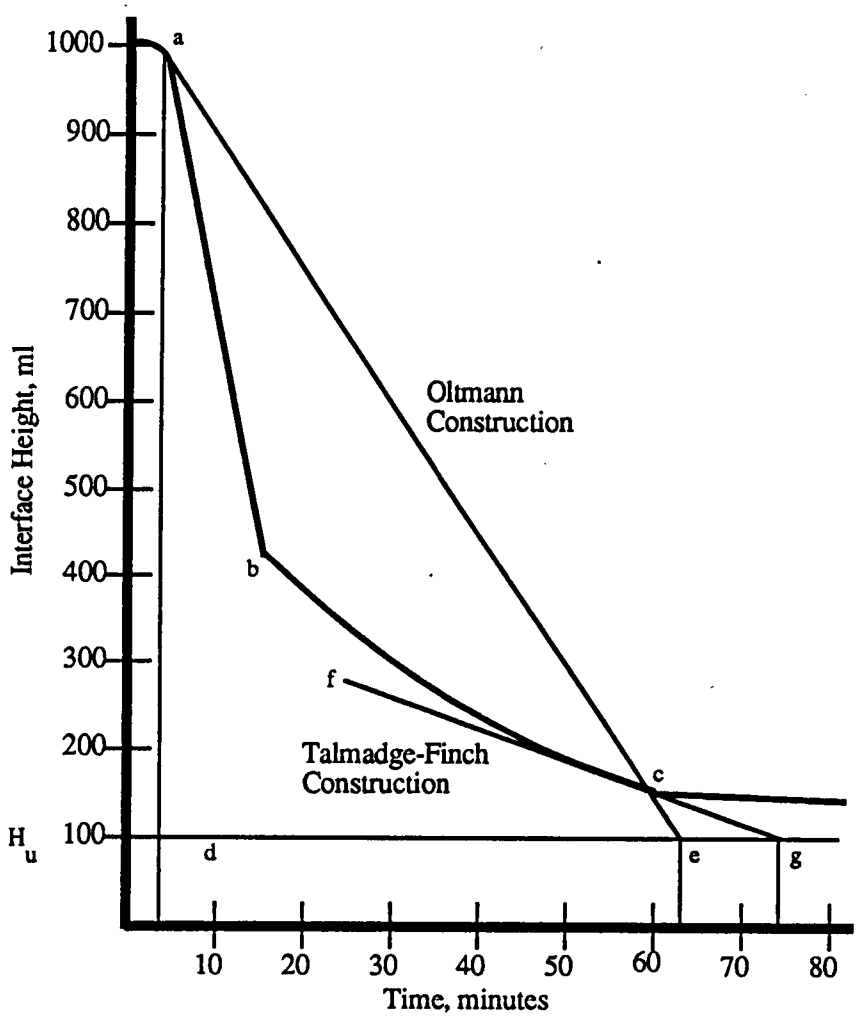

Figure 10. Oltmann and Talmadge-Fitch Constructions [8]

Characterization of Filter Area

In a continuous filter of the rotary drum type, the feed, filtrate, and cake solids move at a constant rate. However, for any particular element of the filter surface, conditions are also transient. The filter goes through a process by which a cake is formed, washed, dried, and discharged. Therefore, the process conditions are constantly changing. The pressure drop across the filter during cake formation is, however, held constant. Thus the equations developed in Chapter III can be modified to reflect the unsteady state operation of a continuous filter.

Using equation 14, the continuous filter system can be represented as:

$$\theta = \left(\frac{\mu r^* C^*}{2P_T}\right) v^2 \tag{26}$$

Note that the second term of equation 14 has been taken to be zero. This is a good assumption if the filter media is washed after the cake is discharged since R_m would tend to be very small. Now solving equation 26 for v:

$$v = \left[\left(\frac{2P_T}{\mu r^* C^*}\right)\theta\right]^{0.5} \tag{27}$$

Division by θ gives:

$$\frac{v}{\theta} = \frac{Q}{A} = \left[\frac{2P_T}{\mu r^* C^* \theta}\right]^{0.5} \tag{28}$$

Equation 28 may be written in terms of the volumetric flow rate Q, and the filter characteristics: drum speed n and total filter area A_T. If the fraction of drum submergence f is defined such that:

$$\theta = \frac{f}{n} \tag{29}$$

and $A/A_T = f$ then equation 28 is rewritten as:

$$\frac{Q}{A_T} = \left[\frac{2P_T f n}{\mu r^* C^*}\right]^{0.5} \tag{30}$$

The total filter area required can therefore be calculated based on experimental data collected by the equation:

$$A_T = \frac{Q}{\left[\frac{2P_T f n}{\mu r^* C^*}\right]^{0.5}} \tag{31}$$

If the specific cake resistance varies according to equation 12, then equation 31 can be written as:

$$A_T = \frac{Q}{\left[\frac{2P_T^{1-s} f n}{\mu r_o^* C^*}\right]^{0.5}} \tag{32}$$

Characterization of Centrifuge Area

Using the expression given in equation 20 of Chapter III, the centrifuge index is given by the equation:

$$\Sigma = \frac{Q}{2v_t} \tag{33}$$

where Σ, the so-called sigma value, is characteristic of the centrifuge, defined as:

$$\Sigma = \frac{Vr\omega^2}{gd_t} \tag{34}$$

Hence, the volumetric flow rate through the centrifuge is written (equation 22) as a function of two parameters, one involving the centrifuge characteristics (Σ), and one involving the particle and fluid properties (v_t). Σ has the dimensions of (length)^2 and is actually equivalent to the area of a settling tank or continuous filter capable of affecting the same level of separation.

It is important to note that the driving force for solid-liquid separation in the case of the centrifuge is $\omega^2 r$ while the driving force in a settler is g. The ratio of $\omega^2 r$ to g is an expression of the increased separation ability of a centrifuge when compared to a settling tank. Therefore, a settler would need an area given as:

$$A = \frac{\omega^2 r}{g}\Sigma \tag{35}$$

to give the same level of separation as a centrifuge with an equivalent area of Σ.

CHAPTER V

EXPERIMENTAL PROCEDURES

Characterization of Spent Seed Material

The spent seed material collected in various downstream particulate control devices of the MHD system is primarily soluble potassium sulfate (Table I). The remaining insolubles (slag) can be characterized as insoluble oxides of silicon, iron, and aluminum, in order of importance. The average particle size for the MHD spent seed material has been determined to be less than one micron in diameter (mass mean diameter (MMD) = 0.77 μm). Due to this fact, the spent seed material represented a considerable problem in solid-liquid separation applications since conventional separation methods depend upon either high terminal velocities (characteristic of larger particles) or upon high filterability (requiring particles of the similar order of magnitude as the pore size of the media to prevent blinding). Neither of these criteria were easily met by the spent seed material characteristic of the MHD process. Because of this, alternate methods were studied to determine the best combination of solid-liquid separation devices which would affect the best possible separation of the insolubles from the soluble fraction.

Table I. Chemical Composition of MHD Spent Seed Material from LMF4-K [2].

Component	Spent Seed (Weight %)
Water Soluble	85.2
SiO_2	5.51
Al_2O_3	1.29
Fe_2O_3	3.94
TiO_2	0.15
CaO	1.04
MgO	0.12
Na_2O	0.44
K_2O	45.3
SO_3	41.3
P_2O_5	0.85
Cl	0.05
Total	100.00

Optional Configurations Considered

Several optional equipment configurations have been considered. The primary equipment item for the separation of the spent seed solubles and insolubles was a settling tank (clarifier). To improve settling rate, different flocculants were studied in various dosages. At the same time, a filter was also evaluated to determine if the spent seed containing dilute slurry could be filtered. Body feeds of diatomaceous earth were used to possibly improve the filtration rate of the slurry. To further dewater the underflow from the clarifier containing spent seed insolubles, two different options were considered: (1) a vacuum filter, and (2) a centrifuging filter. These were thought to be the best options for the proposed solid-liquid separation. Also considered was the option of allowing the underflow to go to the slag leaching system without further dewatering. For the separation of the soluble formate products from the insoluble gypsum, a filter was the obvious choice. Preliminary tests by the UTSI team indicated that the product slurry from the formate reactor would not be difficult to filter. One option that was considered was the use of body feeds or filter precoats to further improve the filtration characteristics. Filter precoats were studied in detail as a better option than body feeds. This was due to the desire to filter the formate containing solution quickly after reaction to prevent the formation of calcium formate by-product.

Parameters Varied

The following parameters were studied in the spent seed solid-liquid separation experiments:

- Equipment- as discussed above.
- Additives- flocculants, filter precoats, and body feeds as required.

- Temperature- in the range of 60 to 95 °C.
- Ratio of K_2SO_4 to H_2O- in the range of 8:100 to 14:100.

Flocculants were provided by the Polymers Division of the Nalco Corporation [14]. The flocculants were polymers of the acrylonitrile group. The ionic nature of the flocculants ranged from highly anionic to cationic with some flocculants of nonionic character. The majority of the flocculants evaluated were of the anionic nature since preliminary tests done by Patil [15] indicated that polymers of anionic nature would perform better. An elevated temperature was chosen due to the increasing solubility of potassium sulfate in water below 200 °C. This allowed a more concentrated solution to be made and could be advantageous downstream of the formate reactor where the products must be dried by evaporation. Additionally, the elevated temperature had an inherent advantage downstream at the formate reactor where temperatures must be in the range of 200 °C. A practical limit of 95 °C was chosen to insure that a pressure vessel would not be required at this stage of processing. At a weight ratio of K_2SO_4 to H_2O of 8:100 the solubility limit of potassium sulfate in water at room temperature is nearly reached. Staying slightly below that limit will insure that potassium sulfate does not leave with the unextracted solids during processing. Elevated temperatures will allow a more concentrated slurry to be used as the solubility of potassium sulfate in water increases dramatically up to 198 °C.

The following parameters have been studied in formate product filtration experiments:

- Various feeds - depending upon whether or not slag was leached and included in the formate product stream.
- Degree of vacuum - 12 to 24 inches Hg.
- Filter precoats - thickness ranging from 0.125 cm to 0.5 cm.

- Cake washing characteristics - extent of potassium recovery from the filter cake as a function of wash volume.

Due to the fact that slag leaching was considered to be optional in the Formate Process concept, two different mixtures were considered for the formate product stream. These were a product stream from the formate reactor without addition of the products from slag leaching and a formate reactor product stream mixed with the slag leaching products in an appropriate ratio. This ratio was determined based on the assumption that for every pound of spent seed produced approximately 0.1421 pounds of slag are produced. Additionally, a selected filter precoat material, Speedex, supplied by the Dicalite Corporation [16] was tested in several different dosages ranging from 2.5 to 10 grams per 62.6 cm^2 filtration area (i.e. 0.04 to 0.16 g/cm^2 surface density). This resulted in a precoat thickness ranging from approximately 0.125 cm to 0.5 cm. The degree of vacuum was varied from 12 to 24 inches of Hg representing a range of approximately 0.4 to 0.8 atmospheres of vacuum. Based on the initial slurry volume, the recovery of soluble potassium from the filter cake obtained from the filtration of the formate product stream was determined as a function of wash liquor volume.

Equipment Used

For settling studies with slurries containing spent seed material, stoppered graduated cylinders (volume=500 ml) were used. The standard equipment item for flocculant testing was the jar test apparatus as shown in Figure 11. Based on standard jar test methodology, the effectiveness of flocculant on settling of spent seed material was evaluated. After the best flocculant was selected, the above mentioned cylinder settling tests were carried out to confirm the results. Filtration experiments were carried out using a bench scale leaf filter supplied

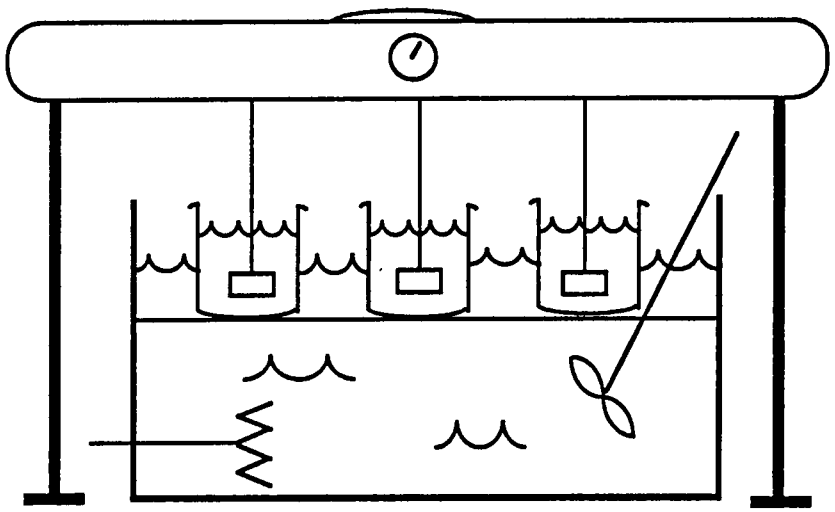

Figure 11. Experimental Apparatus for Jar Testing

by Grefco, Inc. (Figure 12). This filtration unit required a slight modification to provide sufficient support for the filter paper media being used. With the modified unit, the filtration rate could be accurately determined and the degree of vacuum (i.e. pressure drop across the filter cake) varied. A bench scale centrifuge was used to determine the extent to which solid-liquid separation (i.e. dewatering of the underflow material from settling experiments) could be accomplished by centrifugal forces. The centrifuge with an arm length of 14.3 centimeters was capable of speeds ranging from approximately 300 to 2500 RPM. It could hold four standard, graduated separation tubes at the same time.

Experimental Procedure for Spent Seed Settling

Up to three samples were processed simultaneously using the multiple stirrer unit. The procedure used for spent seed dissolution was to place a known amount of spent seed material in the appropriate amount of water at the desired temperature in a beaker. Stirring was initiated and the mixture maintained at the desired temperature using a constant temperature water bath. After approximately 20 minutes the samples were considered to be homogeneous. The contents of the beakers were then transferred to stoppered graduated cylinders. The cylinders were then inverted several times to insure good mixing. The cylinders were placed in a constant temperature water bath maintained at either 60 or 95 °C. The interface height (i.e. demarcation line between the clear supernatant liquid and the insoluble containing bottom fraction) as a function of time was recorded for each sample. At the end of one hour the experiment was stopped and the sample remixed by inverting the cylinder. In this way, each sample could be used for several runs.

The procedure used for the testing of flocculants was based on standard jar

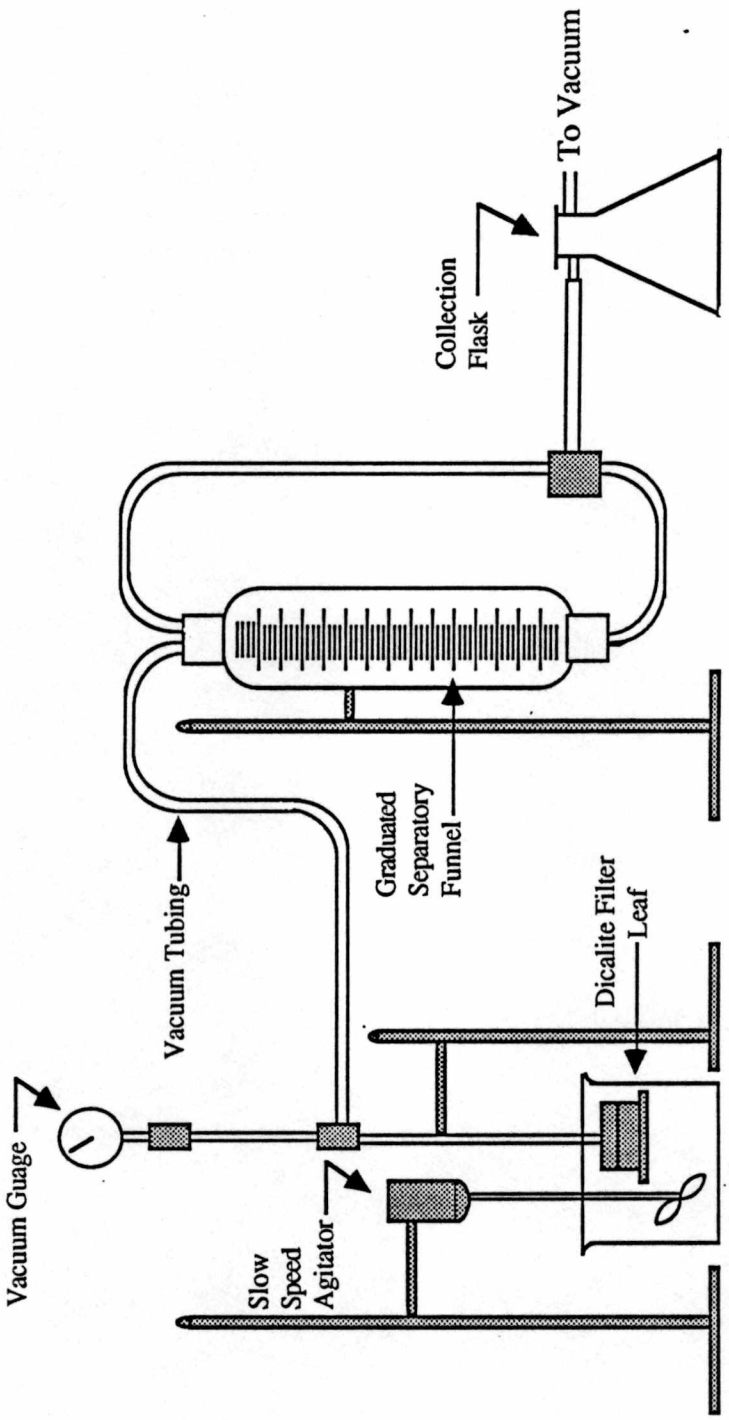

Figure 12. Grefco Bench Scale Leaf Filter [16]

test methodology. Using 500 ml beakers ("jars"), samples of slurry with concentration of 8 parts K_2SO_4 to 100 parts H_2O were mixed with different commercially available flocculants at a 20 ppm dose level. During flocculation, a water bath maintained the temperature of the samples at 60 °C. These conditions were chosen based on the cylinder settling tests performed earlier on untreated (unflocculated) BH/ESP solids. The mixing involved a 1 minute flash at 100 rpm followed by 15 minutes of slow mixing at 35 rpm. This was done to allow the flocculant to first contact the solids and then cause them to agglomerate. The flocculated slurry sample was then allowed to settle for 15 minutes. The clear liquid was withdrawn and filtered to determine insoluble solid carryover. Knowledge of the amount of clear liquid gave a good estimate of the sludge density (based on difference). Using these two parameters, the best flocculant was chosen based on the minimum solid carryover and maximum sludge density. Further tests were completed with the selected flocculant at different dose levels to determine proper dosage. Cylinder settling tests were then carried out to determine the initial settling rate, and to confirm sludge density and solid carryover measurements for the selected flocculant at the proper dosage.

Experimental Procedure for Spent Seed Filtration

Two different types of spent seed slurry have been filtered. Spent seed slurries in concentrations of 8:100 and 14:100 (K_2SO_4:H_2O) have been filtered with and without the aid of flocculants. Additionally, several filtration tests were carried out on spent seed slurry with insoluble solids in approximately a 25 weight percent range. This was thought to be representative of the underflow material/sludge that would be obtained on large scale operations after settling of the spent seed slurries with the appropriate flocculants. Due to the extremely slow rate of fil-

tration obtained for this concentrated sludge, four different dosages of body feed of diatomaceous earths were also tested to improve the porosity of the filter cake. The slurries were placed in a 1000 ml stirred beakers. When using flocculants, the samples were mixed in a manner similar to that outlined above. For the experiments with body feeds, diatomaceous earth of a Perlite type manufactured and supplied by the Grefco Division of the Dicalite Corporation [16] was mixed in an approximately 10 weight percent slurry with water. This additional volume of water used in slurrying the body feed was accounted for when preparing the spent seed slurry samples. Upon addition of the body feed slurry, the samples were stirred until uniform. Vacuum from 12 to 24 inches of Hg was applied to the filter head with a prepared media. The filter head was then immersed in the slurry and a timer started. The volume of liquid collected as a function of time was recorded. At the end of a run (usually when the amount of slurry remaining in the beaker was small), the solids were recovered along with the liquid. These two fractions were remixed in order to be used again if needed. This recycling was not possible when using body feeds due to the addition of the body feed to the starting material.

Experimental Procedure for Spent Seed Centrifugal Separation

To simulate the underflow material typical of commercial operation, a concentrated slurry (25 percent solids by weight) was prepared by settling spent seed with addition of a specified flocculant. This slurry was placed in graduated centrifuge tubes. The samples were then centrifuged to evaluate dewatering by centrifugal separation. The interface height was recorded after centrifuging. The samples were then remixed to be used again. Speeds between 592 rpm and 1954 rpm were studied at centrifuge times ranging from 0 to 40 minutes.

Experimental Procedure for Formate Products Filtration

The slurry samples of formate reactor products maintained at room temperature were placed in a 1000 ml stirred beakers. For the experiments with filter precoats, diatomaceous earth supplied by Dicalite Corporation [16] was mixed in an approximately 10 weight percent slurry with water. This slurry was filtered through the media before using the formate product slurry to provide the necessary thickness of filter precoat. Vacuum from 12 to 24 inches of Hg was applied to the filter head with a prepared media. The filter head was then immersed in the slurry and a timer started. The volume of filtrate collected as a function of time was recorded. At the end of a run (usually when the amount of slurry remaining in the beaker was small), the filter cake and filtrate were collected for the desired analyses.

Experimental Procedure for Formate Products Cake Washing

For cake washing experiments, incremental volumes of deionized water were added to the Buchner funnel containing a representative cake obtained from the filtration experiments with the formate reactor products. After each washing, the liquid collected was raised to a known volume and a sample taken for chemical analysis for potassium content. This was continued until the concentration of potassium in the filtrate liquid was essentially zero as determined by analysis.

CHAPTER VI

RESULTS AND DISCUSSION

This chapter is divided into four major sections. The first section deals with the results obtained from batch settling test performed on spent seed material. Section two presents the results of filtration tests conducted on spent seed slurries. The third section involves the data collected during batch centrifuging test on spent seed slurries. Finally, section four presents data collected on the filtration of the formate containing slurry and mixtures of the product slurries from the formate reactor and the slag digestion systems.

Results of Spent Seed Settling Experiments

Effect of Temperature and Feed Concentration on Settling Velocity

Figure 13 gives a comparison of the settling behavior of untreated spent seed in water at three conditions. Table II gives a comparison of settling velocity, v_s, as a function of the three conditions tested. As expected, feed concentration did not have a significant effect on the settling velocity of the spent seed slurries, while increasing temperature showing a slight decrease in the settling velocity. The temperature should have caused an increase in the settling velocity since the liquid viscosity would have been lowered. However, the cooling and reheating of the sample slurry (brought about by convective heat transfer with the surroundings) created convective currents within the slurry which tend to decrease the solid flux in a downward direction (i.e. the convection is in the upward direction from high density region to a lower density region). These same convective currents exist at lower temperatures (brought on by density differences in the underflow and

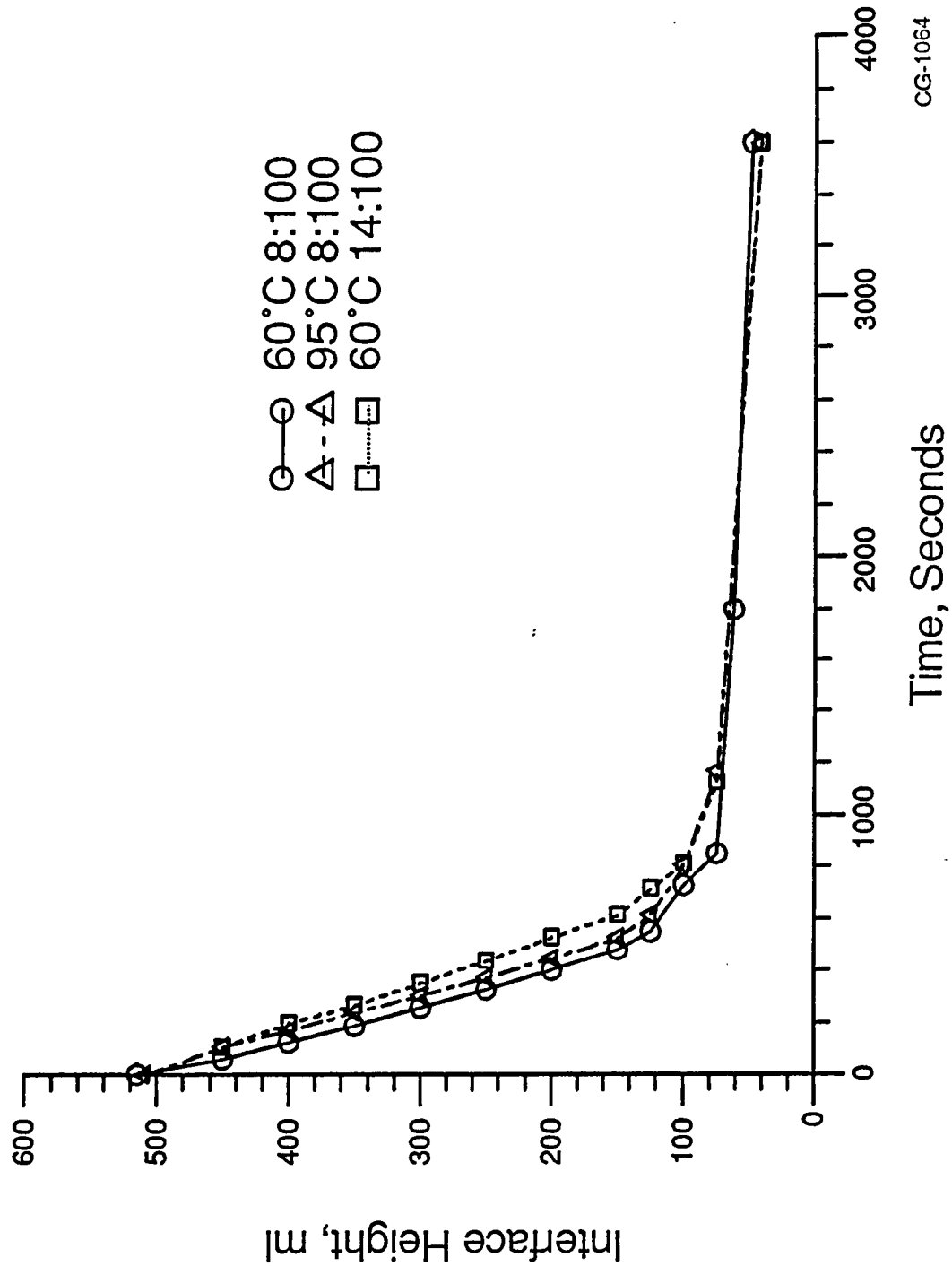

Figure 13. Settling of Untreated Spent Seed at Three Conditions

overflow) but are not as evident. Overflow concentration, C_o, and underflow concentration, C_u, were also affected only by temperature changes. These differences are slight and can be attributed to experimental error.

Table II. Settling of Untreated Spent Seed Material at Three Conditions.

Temperature (°C)	C_f (g/cm^3)	v_s (cm/s)	C_o (g/cm^3)	C_u (g/cm^3)
60	1.46	7.82×10^{-2}	5.28×10^{-5}	0.134
60	2.56	7.72×10^{-2}	5.16×10^{-5}	0.131
95	1.46	6.50×10^{-2}	5.44×10^{-5}	0.162

Determination of Critical Point, Ultimate Time, and Solids Mass Flux

The critical point was easily determined for all tests done on untreated spent seed. As can be seen in Figure 13, the second discontinuity in each case was clearly evident and easily located. Table III gives a summary of the critical times for each of the three settling conditions. Also given are the ultimate times determined by Oltmann and Talmadge-Fitch constructions.

Table III also gives the solids mass flux, G_c, for the three conditions calculated by both the Oltmann and Talmadge-Fitch methods. The mass flux was generally lower than acceptable limits for all conditions. Unit areas required to accomplish the given separation would be on the order of 60 to 100 ft^2 day/ton. At the higher temperature, the mass flux decreased probably due to the convective currents present in the system caused by heating and cooling. This effect was also present

in the 60 °C run but not as evident. The higher concentration run also showed a decrease in the solids mass flux indicative of the increased interaction between particles during settling. Hence, hindered settling for the concentrated system started at an earlier absolute time due to the increased amount of solids per unit volume. In other words, because of the increased solids density, the particles are forced to interact earlier than lower densities would indicate.

Table III. Critical Time, Ultimate Time, and Solids Mass Flux for Untreated Spent Seed at Three Conditions.

Construction Method			*Oltmann*		*Talmadge – Fitch*	
Temp (^oC)	C_f (g/cm^3)	θ_c (s)	θ_u (s)	G_c (g/cm^2s)	θ_u (s)	G_c (g/cm^2s)
60	1.46	860	940	1.83×10^{-4}	1020	1.69×10^{-4}
60	2.56	1150	1220	1.41×10^{-4}	1430	1.20×10^{-4}
95	1.46	1190	1250	1.38×10^{-4}	1460	1.18×10^{-4}

Selection Criteria for Flocculants

The criteria for selection of the most effective flocculant were specified to be maximum underflow concentration C_u and minimum overflow concentration C_o at a given dosage. A cut-off time, i.e. time at which the experiment was halted and the clear liquid separated from the underflow, of 15 minutes was used for all flocculant tests. Generally, the samples had adequately settled within 5 minutes

of the beginning of each test. A summary of the different flocculants tested during this study is presented in Table IV. Generally, the flocculants with weak ionic character performed better than the strongly ionic. Anionic polymers provided the most promising results with an anionic flocculant Nalco 7766 being the best among those tested.

Table IV. Comparison of Performance of Various Flocculants for Settling of Spent Seed.

Basis: C_f = 1.46 g/cm^3

Temperature = 60 °C

Flocculant Dosage = 20 ppm

Cut-off Time = 15 minutes

Flocculant Identification	*Ionic Character*	C_o (g/cm^3)	C_u (g/cm^3)
Nalco 7763	Anionic	1.43×10^{-3}	0.235
Nalco 7129	Nonionic	3.48×10^{-3}	0.258
Nalco 7181	Cationic	4.10×10^{-3}	0.183
Nalco 7182	Cationic	6.22×10^{-4}	0.327
Nalco 7736	Anionic	3.70×10^{-3}	0.280
Nalco 7766	Cationic	1.15×10^{-4}	0.336

Table V presents the results of dosage tests using Nalco 7766, with a graphical representation of the selection criteria in Figure 14. The maximum underflow concentration was attained at approximately 100 ppm dosage of Nalco 7766. The overflow concentration continued to decrease over the range of flocculant dosages tested. The small magnitude of the values obtained indicate that experimental error could be a major factor in this variation. Based on these tests, a dosage of 20 ppm was chosen as an economical optimum. This was due to the diminishing rate of performance increase over the dose of 20 ppm. It is believed that a dose of 20 ppm is sufficient to provide the necessary binding material for most of the small insolubles. Dosages over this add to the amount of excess flocculant present but do not increase the amount of flocculated material significantly.

Table V. Performance of Selected Flocculant Nalco 7766 for Settling of Spent Seed.

Basis: $C_f = 1.46$ g/cm^3

Temperature = 60 °C

Cut-off Time = 15 minutes

Dosage (*ppm*)	C_o (g/cm^3)	C_u (g/cm^3)
10	1.55×10^{-4}	0.280
20	1.15×10^{-4}	0.336
50	1.04×10^{-4}	0.339
100	9.14×10^{-5}	0.342
200	7.45×10^{-5}	0.335

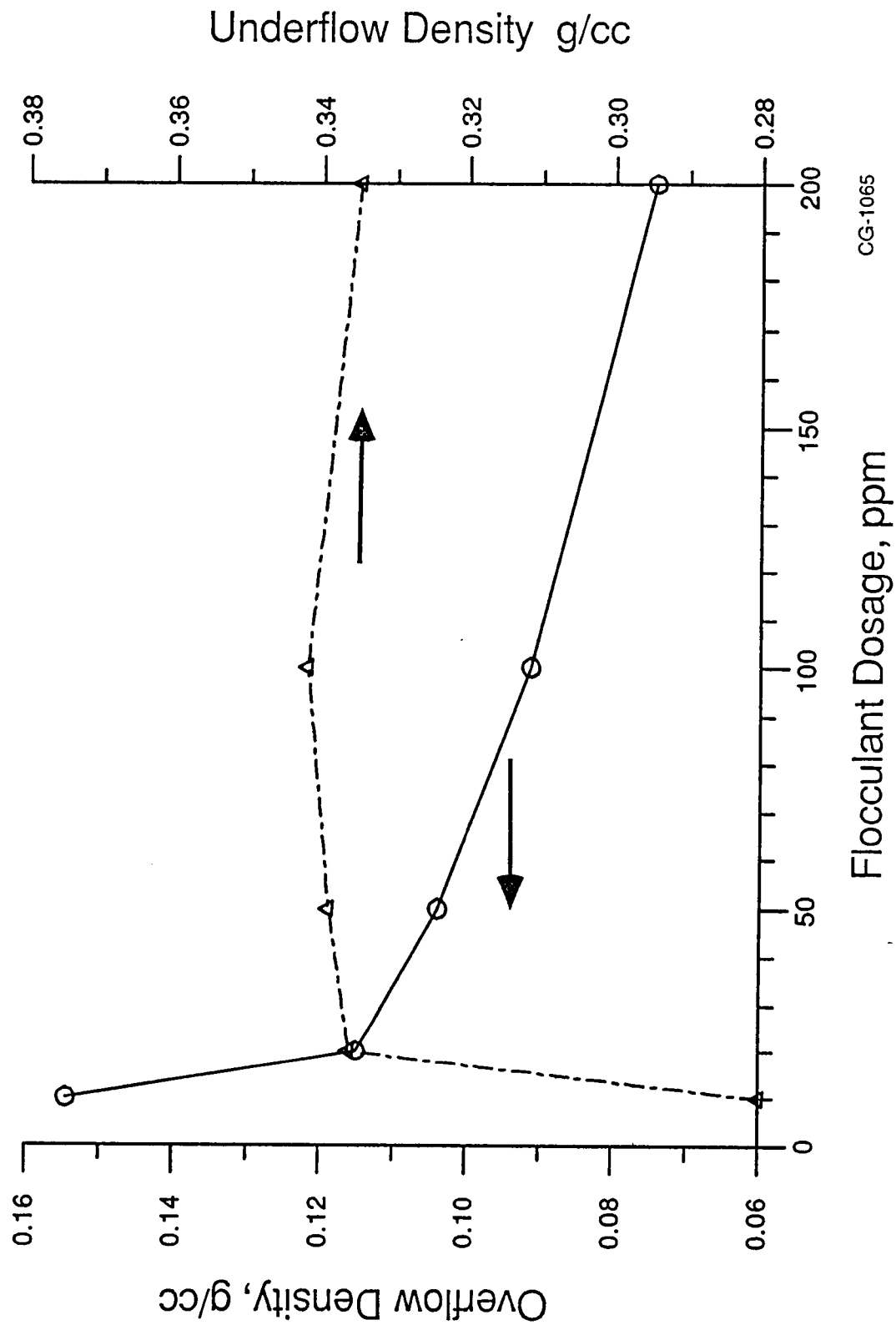

Figure 14. Selection Criteria for Flocculants

Results of Cylinder Tests on Flocculated Spent Seed Settling

Using a 20 ppm dose of Nalco 7766, appropriate cylinder tests were then performed at the three different conditions specified earlier. As can be seen in Figure 15, the settling velocity is nearly identical under all conditions tested. A settling velocity, v_s was calculated to be v_s=0.762 cm/s for all three runs. Therefore, only the base conditions of C_f = 1.46 g/cm^2 and Temperature = 60 ^{o}C were used for calculations. Additionally, the point of second discontinuity in this case is unclear. Because of this, a log-log plot was prepared to determine the critical point (Figure 16.). As can clearly be seen, the second discontinuity occurs at a critical time, θ_c=100 seconds. After determination of the critical time, the mass flux was calculated along with the unit area using both the Oltmann and Talmadge-Fitch methods (Table VI). Generally, the mass flux was an order of magnitude greater than the untreated spent seed slurries had exhibited. This represents approximately a ten-fold decrease in the area of the settler required to affect the same separation.

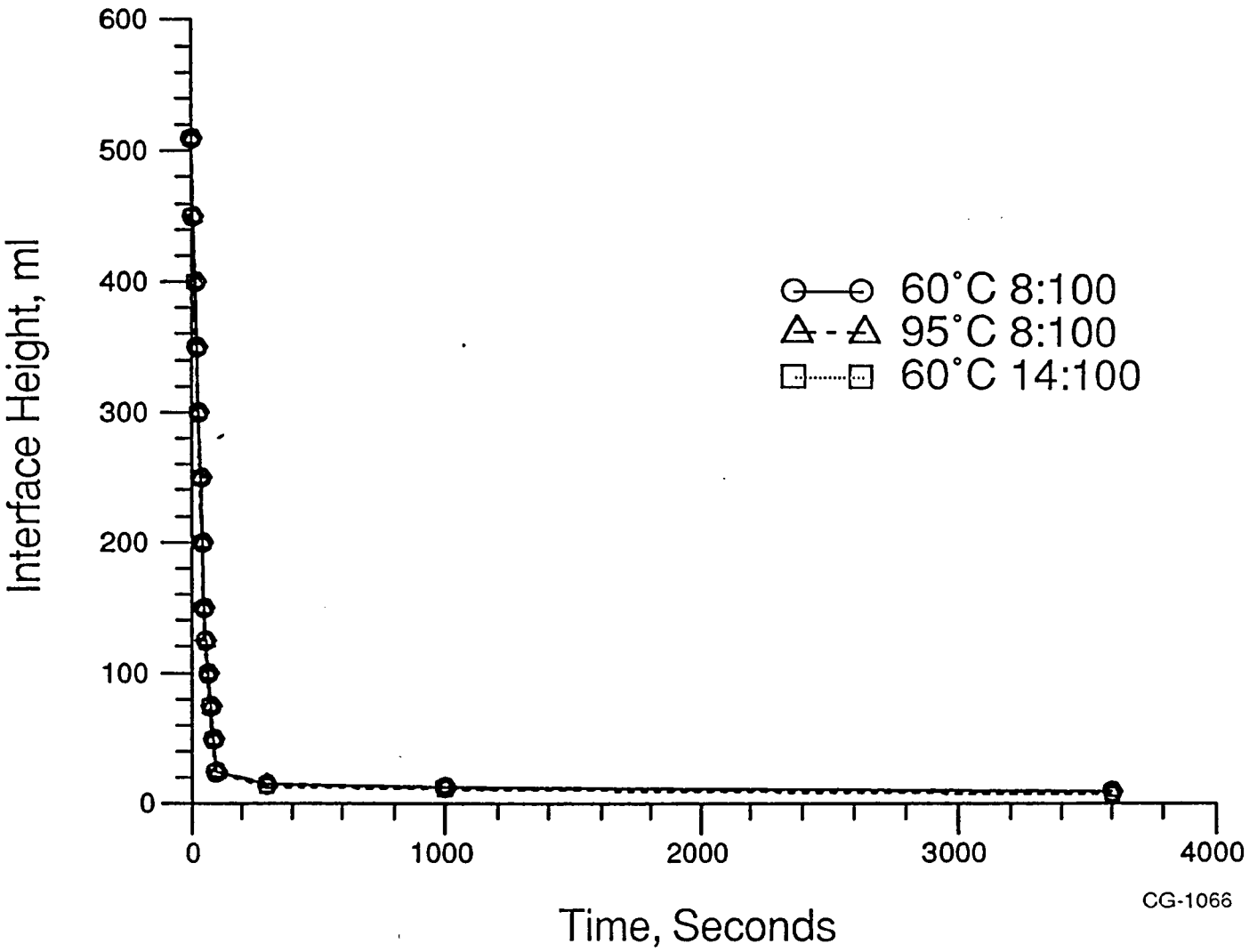

Figure 15. Settling of Treated Spent Seed at Three Conditions

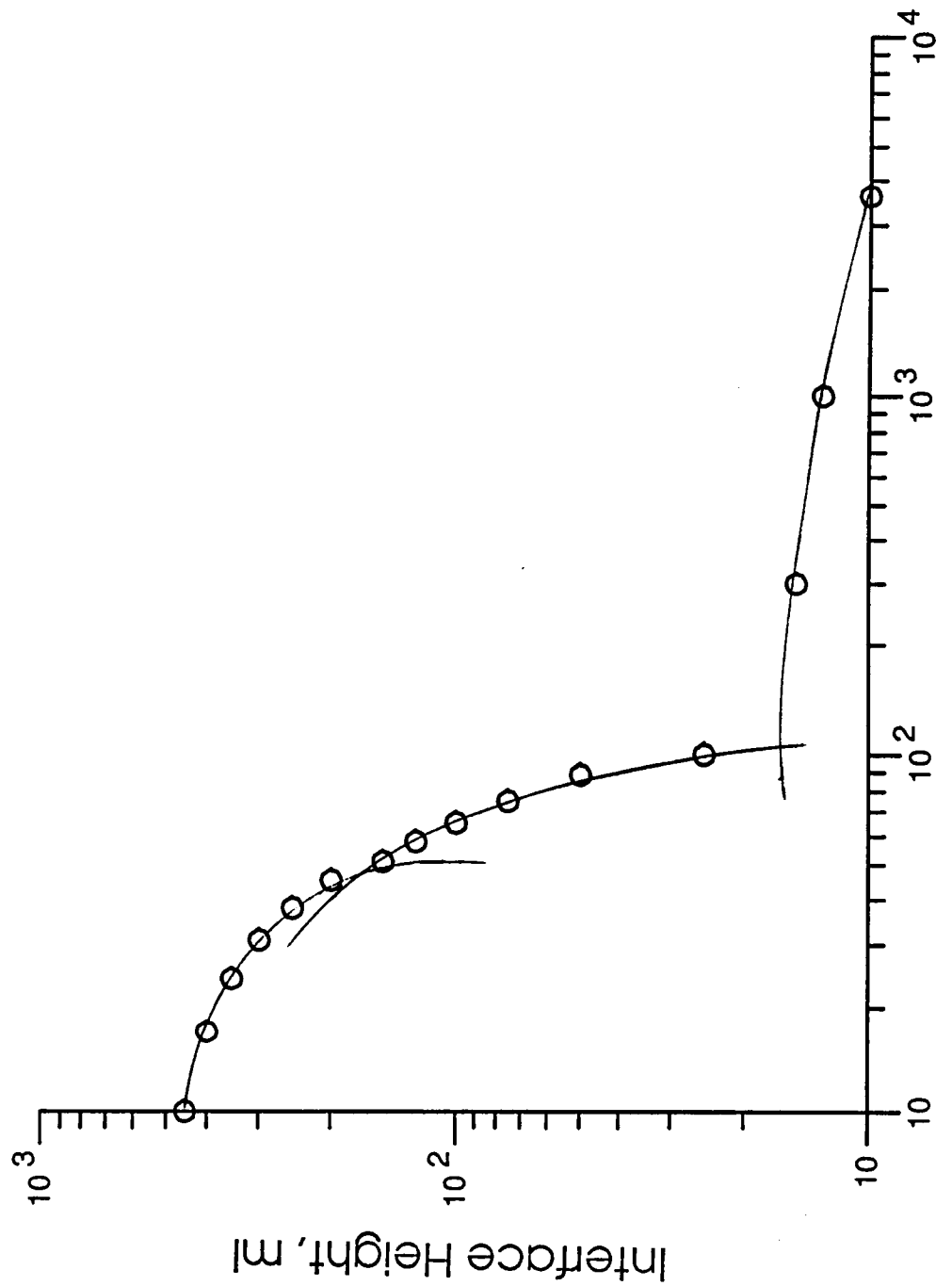

Figure 16. Log-log Plot of Interface Height Versus Time

Table VI. Settling of Flocculated Spent Seed Material.

Basis: $C_f = 1.46$ g/cm^2

Temperature = 60 °C

Oltmann		*Talmadge – Fitch*	
G_c $(g/cm^2\ s)$	$\bar{A}$ $(cm^2\ s/g)$	G_c $(g/cm^2\ s)$	$\bar{A}$ $(cm^2\ s/g)$
1.64×10^{-3}	609.8	1.15×10^{-3}	869.6

Comparison with Other Systems

Table VII gives a comparison of the unit area obtained in settling tests for the flocculated spent seed system with other similar systems. Generally, a unit area in the range of 7 to 10 ft^2 day/ton represents a reasonable system, with unit areas less than 5 ft^2 day/ton being exceptional. Therefore, the performance of the spent seed-water system with flocculation is excellent considering the small size of the particles involved.

Table VII. Comparison of Unit Areas with Literature.

System	C_f (g/cm^3)	$\bar{A}$ (ft^2 day/ton)
Power Plant Flue Dust[17]	1 - 5	2 - 10
Cement Kiln Dust[17]	9 - 10	3 - 18
Spent Seed (This Study)	1.46 - 2.56	6.90 - 9.84

Results of Spent Seed Filtration Experiments

Dilute Spent Seed Slurries

Results of the filtration experiments on spent seed slurries are presented in Table VIII. These are for slurries of feed concentration, C_f=1.46 g/cm^3 and Temperature=60°C. Average filtration velocities ranged from 3.056 $\times 10^{-3}$ to 4.313 $\times 10^{-3}$ cm^3/cm^2 s for untreated solids while rates for the samples treated with Nalco 7766 (the flocculant most effective for settling) ranged from 5.399 $\times 10^{-3}$ to 8.659 $\times 10^{-3}$ cm^3/cm^2 s (for doses from 20 to 100 ppm). For another flocculant, Nalco 7181, the average filtration velocities ranged from 1.745 $\times 10^{-2}$ to 1.138 $\times 10^{-2}$ cm^3/cm^2 s. This represented a considerable increase in the rate of filtration from the untreated samples. The time-volume relationship for each system at three different degrees of vacuum is presented in Figures 17 and 18. As expected, the filtration rate increased with increasing vacuum within the range studied here. Also, increasing dosage of flocculants brought about an increased rate of filtration. This is due to the increased average particle size (brought about by flocculation) which would make the cake more porous. A further indication of the increased porosity of the flocculated cake is given by the decreased cake resistance (Table VIII).

Table VIII. Summary of Results of Filtration Experiments on Dilute Spent Seed Slurries.

Basis: $C_f = 1.46$ g/cm^3

Temperature = 60 °C

Flocculant Identification	Pressure Drop (in. Hg)	Filtration Velocity (cm^3/cm^2 s)	True Specific Resistance, r* (cm/g)
none	24	4.3×10^{-3}	2.0×10^{-10}
none	18	3.9×10^{-3}	1.7×10^{-10}
none	12	3.1×10^{-3}	1.4×10^{-10}
20 ppm Nalco 7766	24	5.4×10^{-3}	1.6×10^{-10}
50 ppm Nalco 7766	24	7.6×10^{-3}	1.1×10^{-10}
100 ppm Nalco 7766	24	8.7×10^{-3}	9.8×10^{-11}
20 ppm Nalco 7181	24	1.1×10^{-2}	7.5×10^{-11}
50 ppm Nalco 7181	24	1.5×10^{-2}	5.6×10^{-11}
100 ppm Nalco 7181	24	1.7×10^{-2}	3.1×10^{-11}

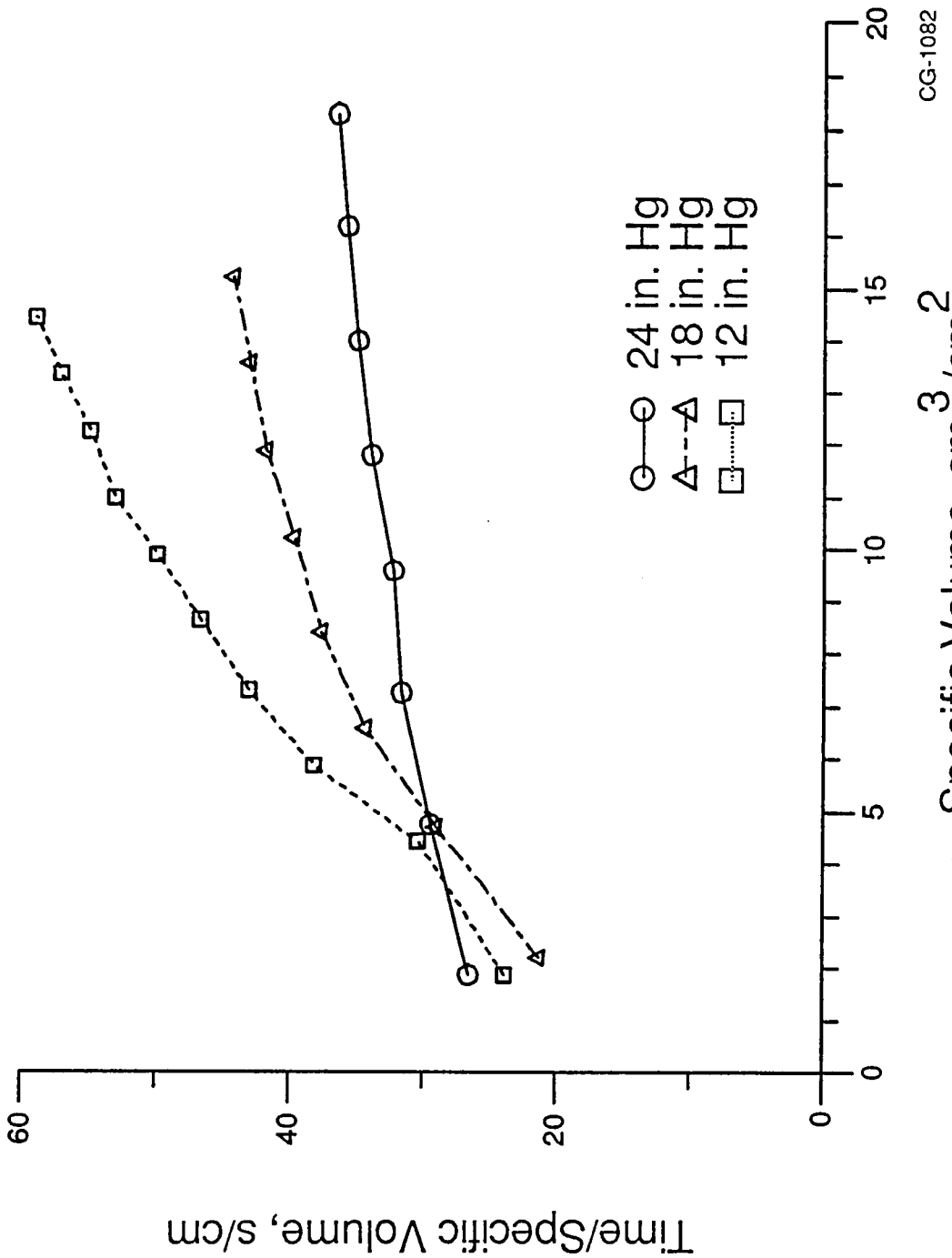

Figure 17. Filtration of Untreated Spent Seed

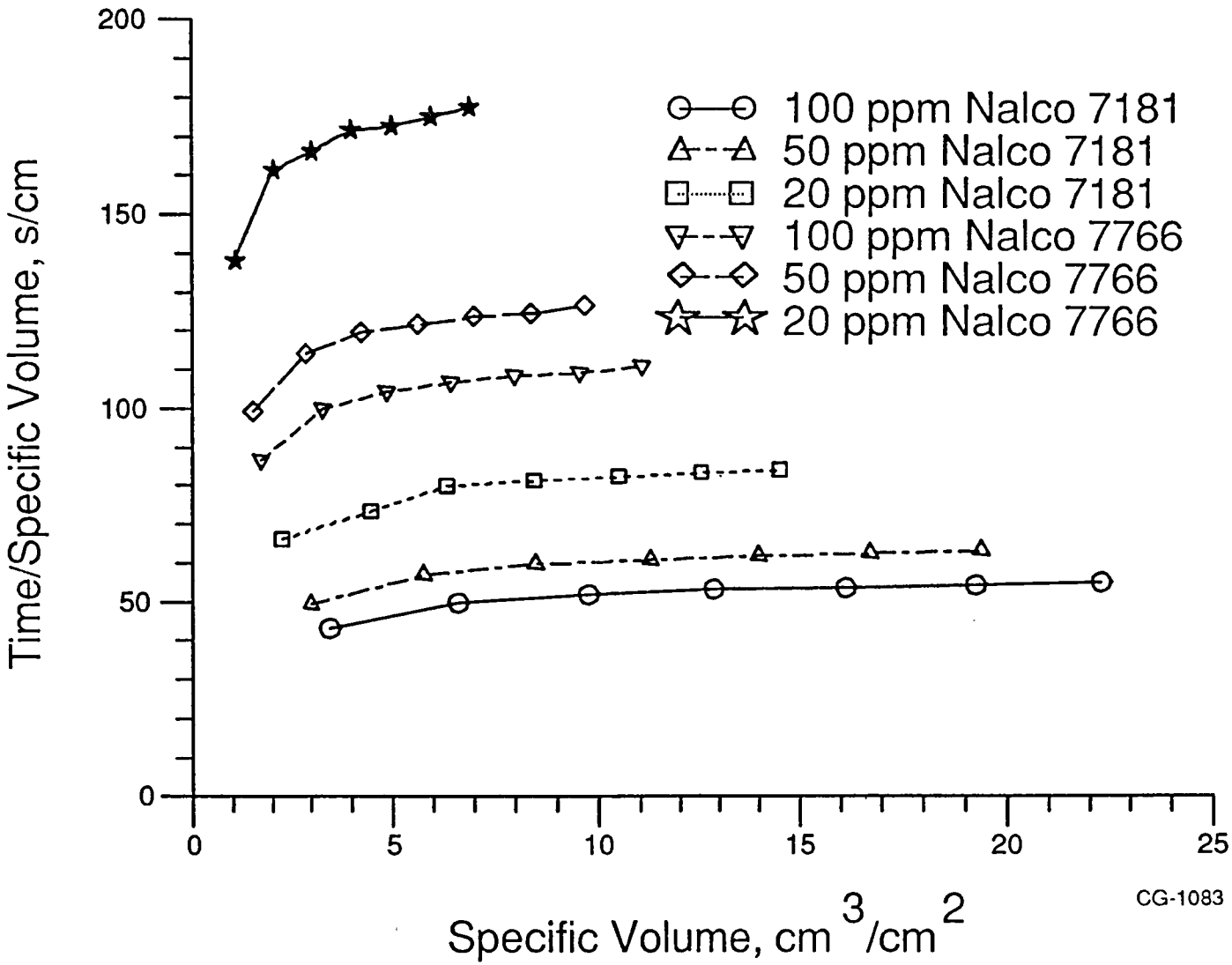

Figure 18. Filtration of Spent Seed Treated with Various Flocculants

Determination of Cake Compressibility Factor for Dilute Slurry Filtration

Figure 19 gives a plot of true specific cake resistance versus pressure drop for the untreated dilute slurry. From this, the cake compressibility factor, s, was determined to be s=0.50. This indicates that a slightly compressible cake was formed. The initial cake resistance, r_o^* was calculated from the plot as r_o^*=4.0 $\times 10^{-10}$ cm/s. For the flocculant treated samples, the cake compressibility could not be determined due to a lack of proper data on the effect of pressure drop across the media. The cake compressibility is however expected to be somewhat lower as indicated by the higher filtration velocities encountered.

Concentrated Spent Seed Slurries

For the concentrated slurry obtained by settling of spent seed with an appropriate flocculant (20 ppm Nalco 7766), a feed concentration, C_f = 25 g/cm^3 was used to simulate the underflow from a settler. This was considerably lower than predicted by the settling experiments. However, RCC [18] felt that this concentration would more accurately represent the underflow from a real full scale settler. The rate of filtration was poor ranging from 7.90 $\times 10^{-4}$ to 1.3 $\times 10^{-3}$ cm^3/cm^2 s at 24 inches Hg vacuum (Table IX). Corresponding cake resistances as shown in Table IX were much higher than expected. Performance with body feeds representing 2,4,6, and 10 percent body feed per solution weight at 24 in Hg vacuum did not show any improvement. In fact, at higher dosages (6 and 10 percent), the performance was greatly degraded with filtration rates around 2.0 $\times 10^{-4}$ cm^3/cm^2· s being encountered. It is possible that the body feed actually served to change the cake porosity causing the resistance to flow to be higher. Alternatively, the agglomerates formed during flocculation could have been unstable

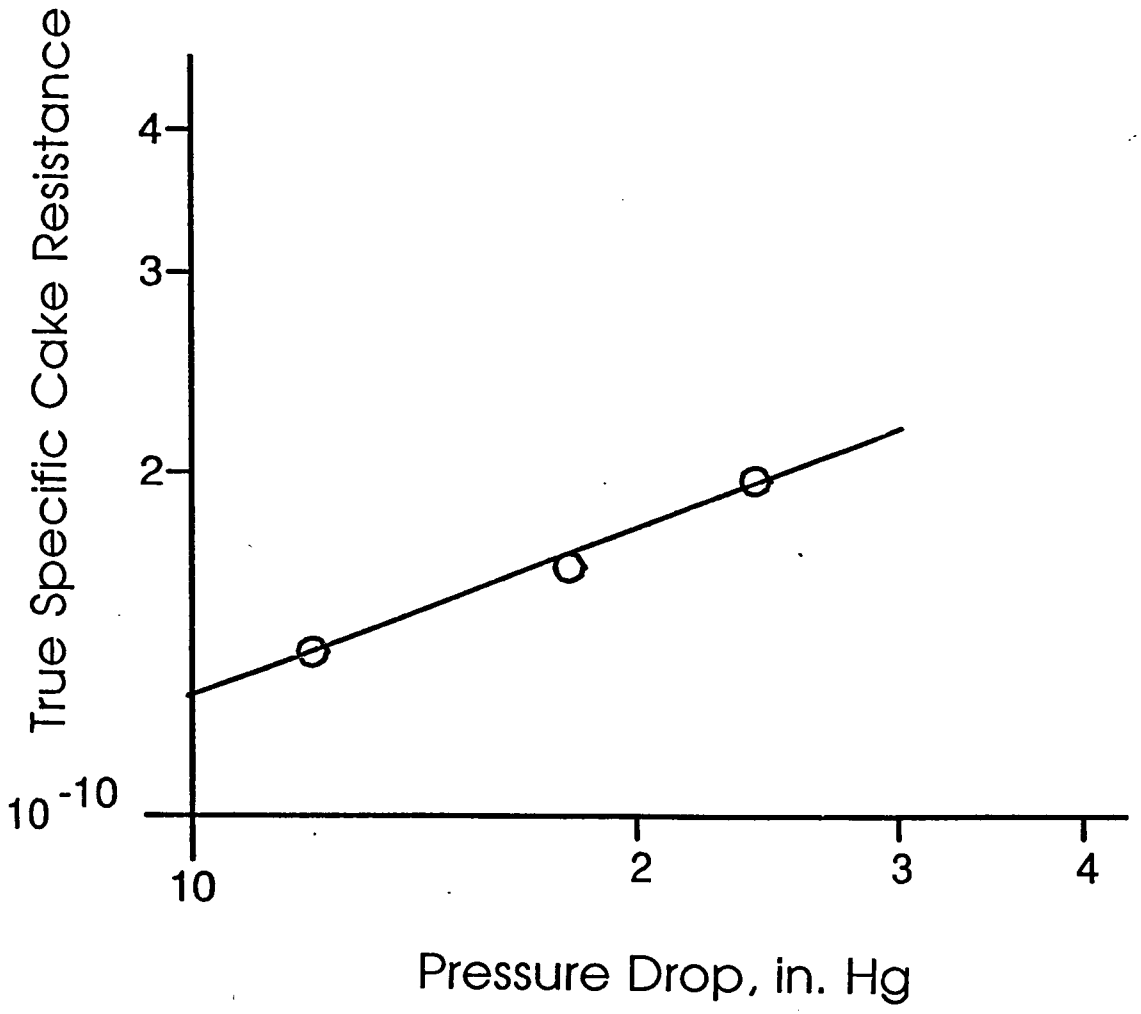

Figure 19. True Specific Cake Resistance Versus Pressure Drop

at this higher body feed concentration (and the resulting mixing) and therefore more easily broken down causing the filtration rate to be lowered. Excessive mixing and transfer of the solids containing slurry could also have contributed to the breakdown of agglomerates.

Table IX. Summary of Results of Filtration Experiments on Concentrated Spent Seed Slurries.

Basis: $C_f = 25.0$ g/cm^3

Temperature = 60 °C

Body Feed	Pressure Drop (in. Hg)	Filtration Velocity (cm^3/cm^2 s)	True Specific Resistance, r* (cm/g)
none	24	1.3×10^{-3}	8.6×10^{-9}
none	18	1.1×10^{-3}	7.8×10^{-9}
none	12	7.9×10^{-4}	7.1×10^{-9}
0.02 % Speedex	24	5.5×10^{-4}	2.0×10^{-8}
0.04 % Speedex	24	6.4×10^{-4}	2.4×10^{-8}
0.06 % Speedex	24	2.3×10^{-4}	4.9×10^{-8}
0.10 % Speedex	24	2.0×10^{-4}	5.5×10^{-8}

Determination of Cake Compressibility Factor for Concentrated Slurry Filtration

The cake compressibility factor for the concentrated spent seed slurry without body feed was determined to be s=0.28 (It is important to note that these samples were previously treated with Nalco 7766 in a 20 ppm dose). In contrast to the value obtained for the dilute slurry (untreated), the filter cake from the concentrated slurry showed a higher degree of incompressibility. Obviously, the concentrated slurries (due to the prior flocculation) would have a higher compressibility due to the agglomeration of solids creating a more porous material. The concentrated slurries treated with body feeds of diatomaceous earth (after flocculation) did not perform as expected possibly due to either a breaking down of the flocculated particles by the mixing process or compression of the solids.

Results of Spent Seed Centrifugal Separation Experiments

The feed stream for the centrifuge with concentration $C_f = 25.0$ g/cm^3 was obtained from settling spent seed slurries flocculated with Nalco 7766. Experiments using the bench scale centrifuge indicated that up to 72 percent of the liquid remaining in the simulated underflow sludge from a settler can be recovered (Table X). This additional liquid recovery amounts to recovering potassium as potassium sulfate which would otherwise be lost or not desulfurized.

Table X. Liquid Recovery By Centrifuging as a Function of Time and Tangential Velocity.

Tangential Velocity (cm/s)	Time (minutes)						
	2	4	6	8	10	20	40
5.50 $\times 10^4$ (592 RPM)	9.16	33.14	38.95	45.49	46.22	56.40	63.66
1.23 $\times 10^5$ (886 RPM)	14.97	46.95	53.49	57.85	59.30	65.10	-
2.13 $\times 10^5$ (1164 RPM)	57.85	60.76	63.66	-	68.02	70.93	-
4.30 $\times 10^5$ (1655 RPM)	62.21	62.21	63.66	68.02	-	68.02	-
6.00 $\times 10^5$ (1954 RPM)	62.94	63.66	-	-	71.66	72.38	-

Determination of Equivalent Area

The equivalent area of the centrifuge was determined using equation 33 of Chapter IV. Table XI gives the centrifuge area divided by the volume of the bench scale centrifuge used. From Tables X and XI, once the liquid recovery and the required residence time are specified, the tangential velocity will be known. The required centrifuge size (i.e. Σ/V) is therefore specified. A comparison of areas for the settler and centrifuge was not possible in this case since the centrifuge and settling experiments were conducted at different conditions (i.e. different feed concentrations).

Table XI. Equivalent Area of Centrifuge Based on Experimental Results.

Tangential Velocity (cm/s)	Σ/V (cm^2/cm^3)	Σ/V (ft^2/ft^3)
5.50×10^4	186.6	6.12
1.23×10^5	417.4	13.69
2.13×10^5	722.8	23.71
4.30×10^5	1459.2	47.87
6.00×10^5	2036.1	66.81

Choice of Type of Centrifuge

The type of centrifuge to use for the given separation of insoluble spent seed from the soluble fraction in a concentrated slurry (C_f = 25.0 g/cm^3) was determined by comparison of the equivalent area divided by volume obtained with literature values [19]. As can be seen in Table XII, three types of centrifuges have been considered: (1) tubular bowl, (2) disc, and (3) a solid bowl basket. The operation of the tubular bowl is generally a batchwise process in that the solids are not discharged from the bowl during operation. The liquid fraction is removed through an overflow port in the top of the tube. This type of centrifuge would be best suited to processes were the liquid is the only desired recovered product. Tubular centrifuges also typically operate in the higher speed ranges (5000 to 15000 RPM). The disc centrifuge is commonly thought to be a rotating settling chamber. The discs serve to decrease the settling distance so that a higher efficiency at lower speeds can be obtained. (Lower speeds also correlate to a lower area to volume ratio). This device is also primarily a liquid recovery type device. A solid bowl basket type centrifuge is a high speed device well suited to continuous operation since the solids are removed through vanes in the side of the basket or bowl. With the higher speed operation (and therefore higher area to volume ratio) the solid bowl basket type centrifuge is best suited to the range of operation desired based on experimental results. Due to the high efficiency of all of the centrifuge types considered ($\geq$99 percent), efficiency was not a factor in the selection of the basket type centrifuge. Additionally, the cost of the centrifuge, because of the small throughput and therefore low cost, was not considered as a factor for selection.

Table XII. Comparison of Equivalent Area for Selection of Centrifuge.

Type of Centrifuge	Σ/V (cm^2/cm^3)
Tubular Bowl[19]	115 - 1050
Disc[19]	3 - 26.5
Solid Bowl Basket[19]	105 - 3000
This Study	186.6 - 2036

Results of Filtration Experiments on Formate and Slag Products

Formate and Slag Products Filtration without Precoats

The results of filtration experiments on formate and formate/slag mixtures are shown in Table XIII and Figures 20 and 21. Filtration rates for formate reactor products ranged from 1.3×10^{-2} to 2.4×10^{-2} cm^3/cm^2 s. As expected,the filtration rate increased with increased vacuum. The addition of slag products increased the filtration rate to some degree (rates from 1.2×10^{-2} to 2.7×10^{-2} cm^3/cm^2 s). This was expected due to the excess lime used in the slag digestion process which will be insoluble. The lime characteristically will be larger particles which will prevent the media from being blinded and provide a more porous cake, thus improving the overall filtration rate. The limiting factor seemed to be the pore size of the media (diameter=0.45 microns) as opposed to the particle size of the insolubles. It is expected that at the proof-of-concept (POC) scale a larger filter media pore size will have a lower media resistance which will result in a greater rate of filtration.

The specific resistances were lower for the tests conducted with Formate/Slag mixtures as expected. This indicates, as stated previously, that the porosity of the cake was increased by the addition of the slag product stream. This conclusion is logical because the slag product stream contains a number of larger particles which would tend to form a more porous cake; thus increasing the rate of filtration (i.e. decreasing the specific resistance).

Table XIII. Summary of Filtration Experiments on Formate and Slag Digestion Products.

Basis: Temperature = 25 °C

Description of Feed	Pressure Drop (in. Hg)	Filtration Velocity (cm^3/cm^2 s)	True Specific Resistance, r* (cm/g)
Formate Products	24	2.4×10^{-2}	1.8×10^{-11}
Formate Products	18	1.9×10^{-2}	2.3×10^{-11}
Formate Products	12	1.3×10^{-2}	3.3×10^{-11}
Formate/Slag Products †	24	2.7×10^{-2}	1.6×10^{-11}
Formate/Slag Products †	18	1.9×10^{-2}	2.4×10^{-11}
Formate/Slag Products †	12	1.2×10^{-2}	3.6×10^{-11}

† Formate/Slag Products are a mixture of the Formate reactor product stream and the Slag leaching product in the appropriate ratio to simulate operation of a full-scale plant.

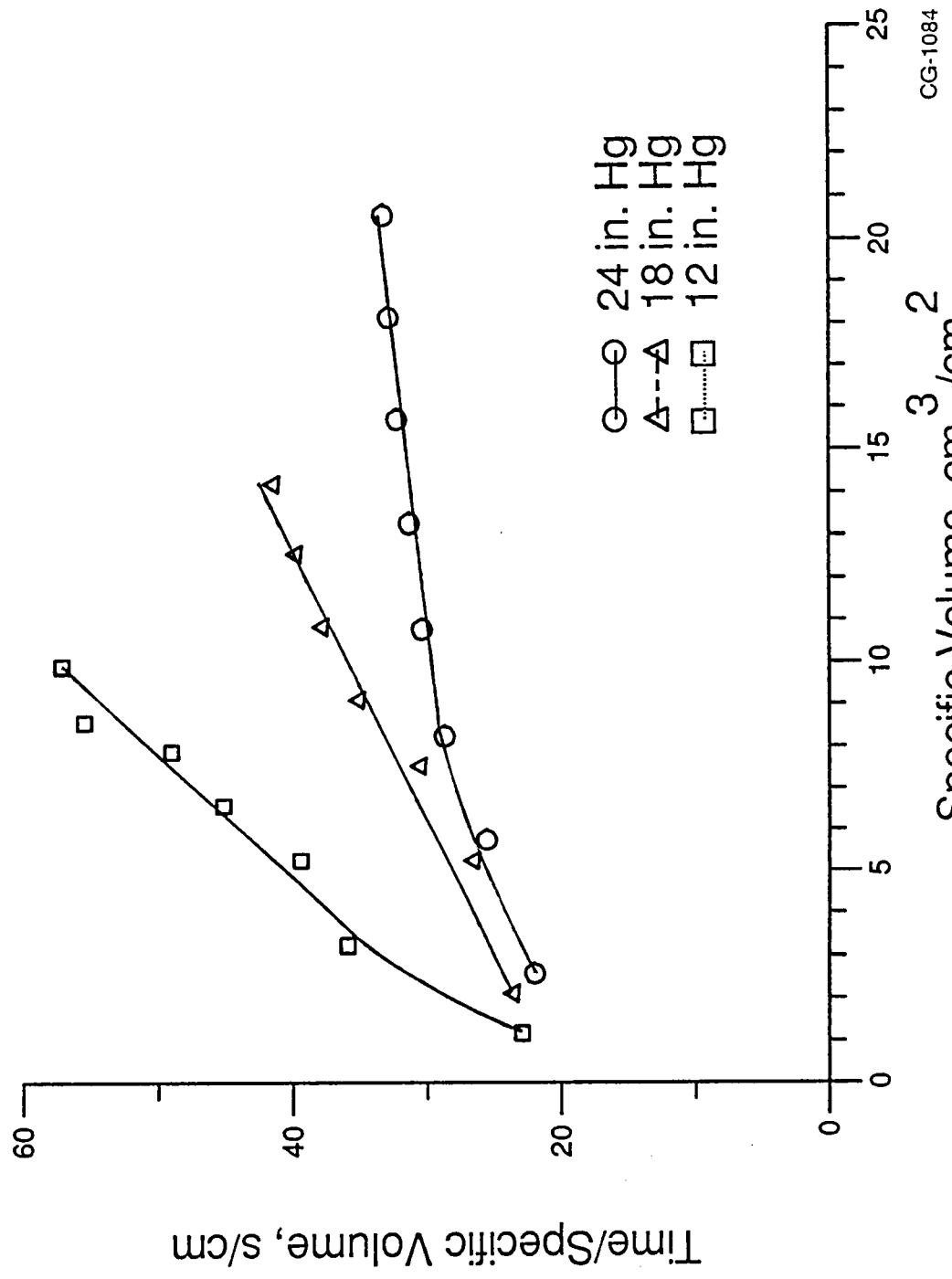

Figure 20. Filtration of Formate Products

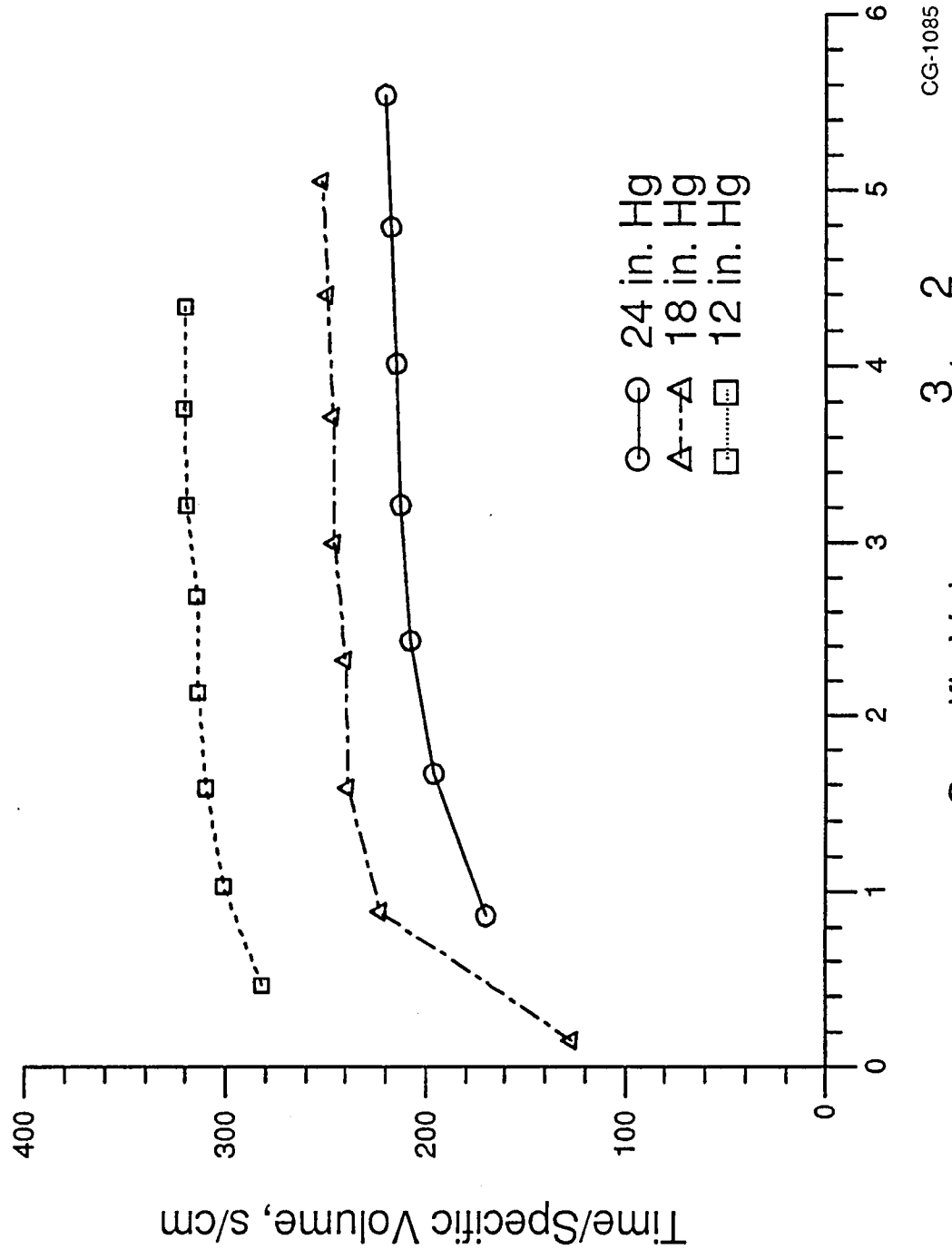

Figure 21. Filtration of Formate/Slag Products

Determination of Cake Compressibility Factor

The cake compressibility factors for both the Formate Product and Formate/Slag Product systems were determined by log-log plotting of specific resistance versus pressure drop. For the Formate Product system without addition of slag leaching products, the cake compressibility was found to be s=0.13. The compressibility factor for the Formate/Slag product system was also s=0.13. Since these values are identical, the addition of the slag digestion products evidently does not degrade the filtration characteristics of the Formate reactor products. The initial cake specific resistance, r_o^* in both cases averaged around 1.2 $\times 10^{-11}$ cm/s.

Formate and Slag Products Filtration with Precoats

As expected, filter precoats deterred filter blinding resulting in a higher rate of filtration . Increasing amounts of precoats were used up to a practical thickness limit of one-half centimeter. Filter precoats in an amount sufficient to give a precoat thickness of approximately 0.50 cm were found to increase the filtration rate by approximately 50 percent (Table XIV and Figure 22) when compared with the tests on an untreated media. The specific resistance to flow was found to decrease with increasing precoat thickness as expected. Due to the fact that the specific resistance was determined from flow measurement, the true specific resistance as given in Table XIV includes the resistance of the precoat. If possible, a blank slurry (containing only precoat material) could have been filtered to determine the contribution of the precoat material to the overall specific resistance. This resistance would be expected to be approximately zero ($r_{pc}^* = 0$).

Table XIV. Summary of Filtration Experiments on Formate/Slag Products with Precoats.

Basis: Temperature = 25 °C

Pressure Drop = 24 in. Hg

Filter Precoat	Precoat Thickness (cm)	Filtration Velocity (cm^3/cm^2 s)	True Specific Resistance, r* (cm/g)
5.0 grams Speedex †	0.250	2.9×10^{-2}	1.5×10^{-11}
7.5 grams Speedex †	0.375	3.3×10^{-2}	1.3×10^{-11}
10.0 grams Speedex †	0.500	3.5×10^{-2}	1.3×10^{-11}

† Speedex is a registered tradename of the Grefco Division of the Dicalite Corporation.

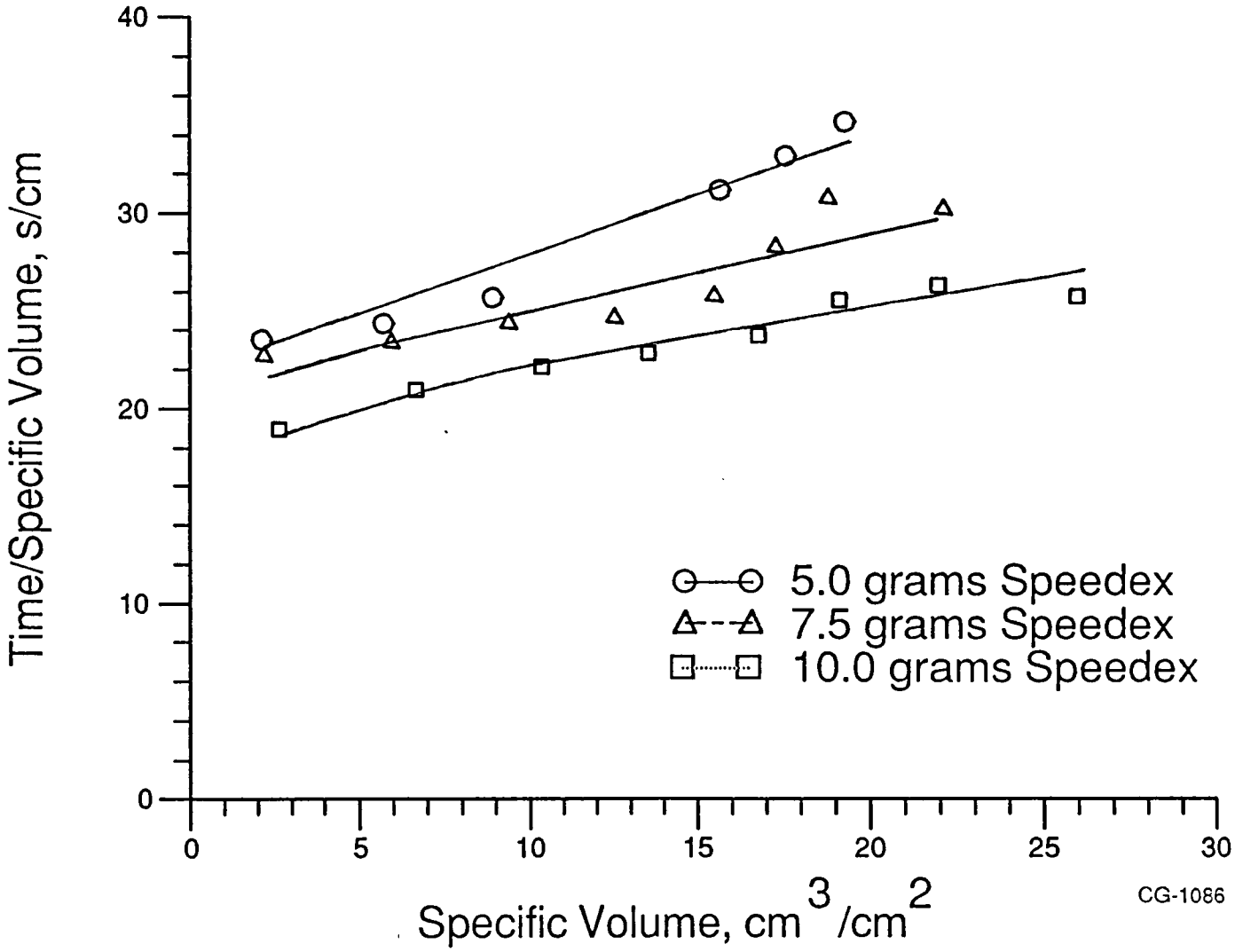

Figure 22. Filtration of Formate/Slag Products Using Precoats

Washing Characteristics of Formate/Slag Products

The results of the washing experiments show that a wash volume of approximately 5 to 10 percent of the initial slurry volume will be needed for 99 percent recovery of the soluble potassium from the filter cake obtained from the filtration of the formate/slag mix (Figure 23). This will correspond to an additional 3.5 percent recovery of the soluble potassium contained in the filter cake when compared with an unwashed cake.

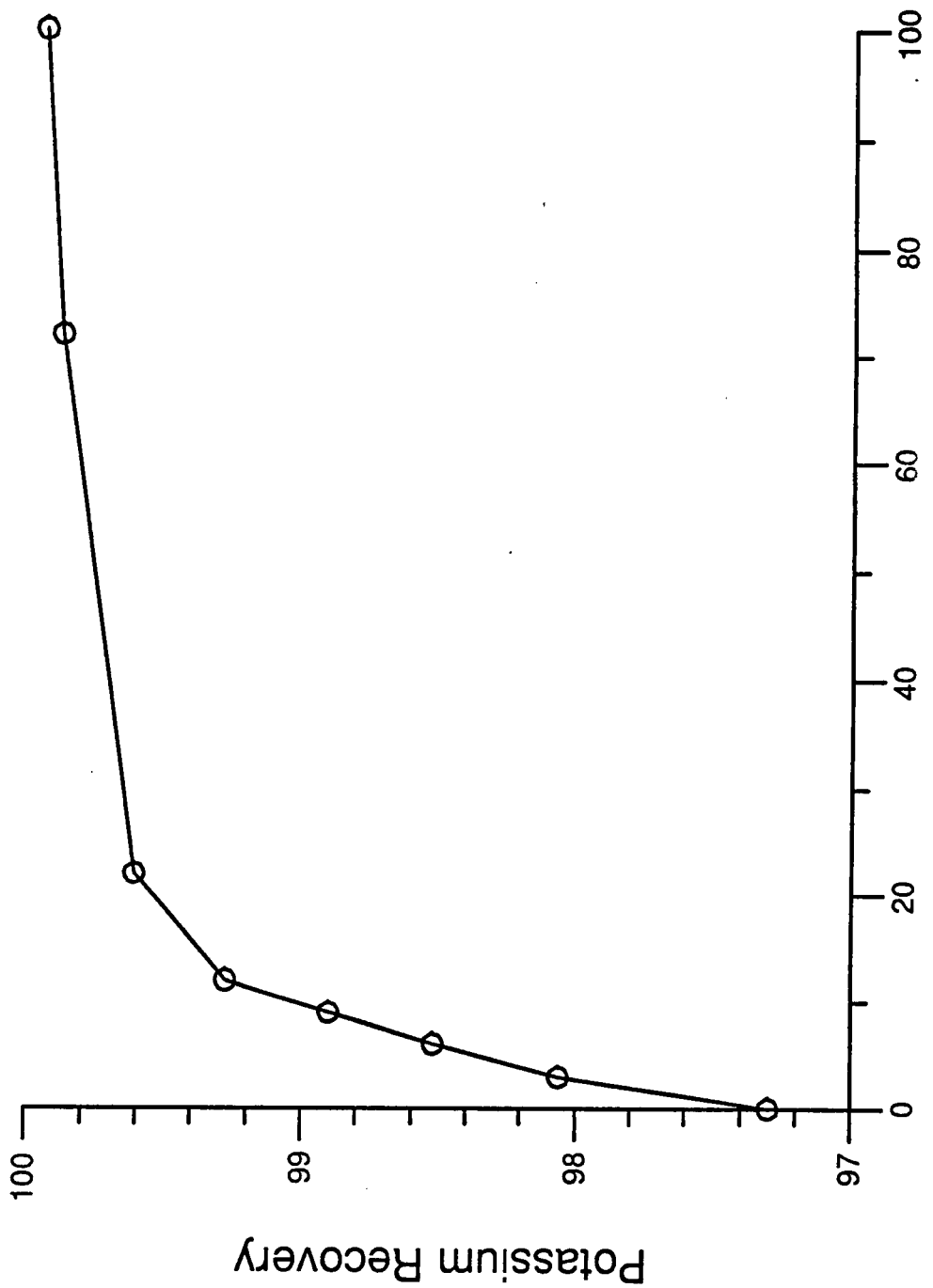

Figure 23. Washing Characteristics of Formate/Slag Products Cake

CHAPTER VII

PROCESS DESIGN AND ECONOMICS

Choice of a System for Spent Seed Solid-Liquid Separation

Based on the experimental results presented in Chapter VI, the system chosen for the solid-liquid separation of the spent seed material was the configuration of a settler followed by a filtering centrifuge. The experimental data showed that a standard filter would not provide a sufficient driving force to separate the insolubles from a dilute slurry containing soluble potassium sulfate in a reasonable time frame. Therefore, a settler was chosen as the best alternative to treat the initial dilute slurry. Additionally, the use of an anionic flocculant, Nalco 7766, in a dosage of 20 ppm was shown to be the best of the flocculants tested at improving the mass flux and thus reducing the size of the settling tank required. Further tests with the selected flocculant above the 20 ppm dose did not make a noticeable improvement in the overall settling rate. Following the settler, a centrifuging filter was determined to be the best alternative for further dewatering of the underflow sludge. Based on the experimental results, a filter would not perform well even with the use of body feeds of diatomaceous earth for dewatering of this sludge. Additionally, the presence of body feed material in the slag (to the slag digestion reactor) may not be allowed.

The Settler-Centrifuge System

Figure 24 gives a process flow diagram of the Settler-Centrifuge system. As can be seen, a slurry of spent seed in water (concentration = 14:100 K_2SO_4:H_2O) at 95 °C will be fed to a mixing tank. In this tank, the anionic flocculant Nalco

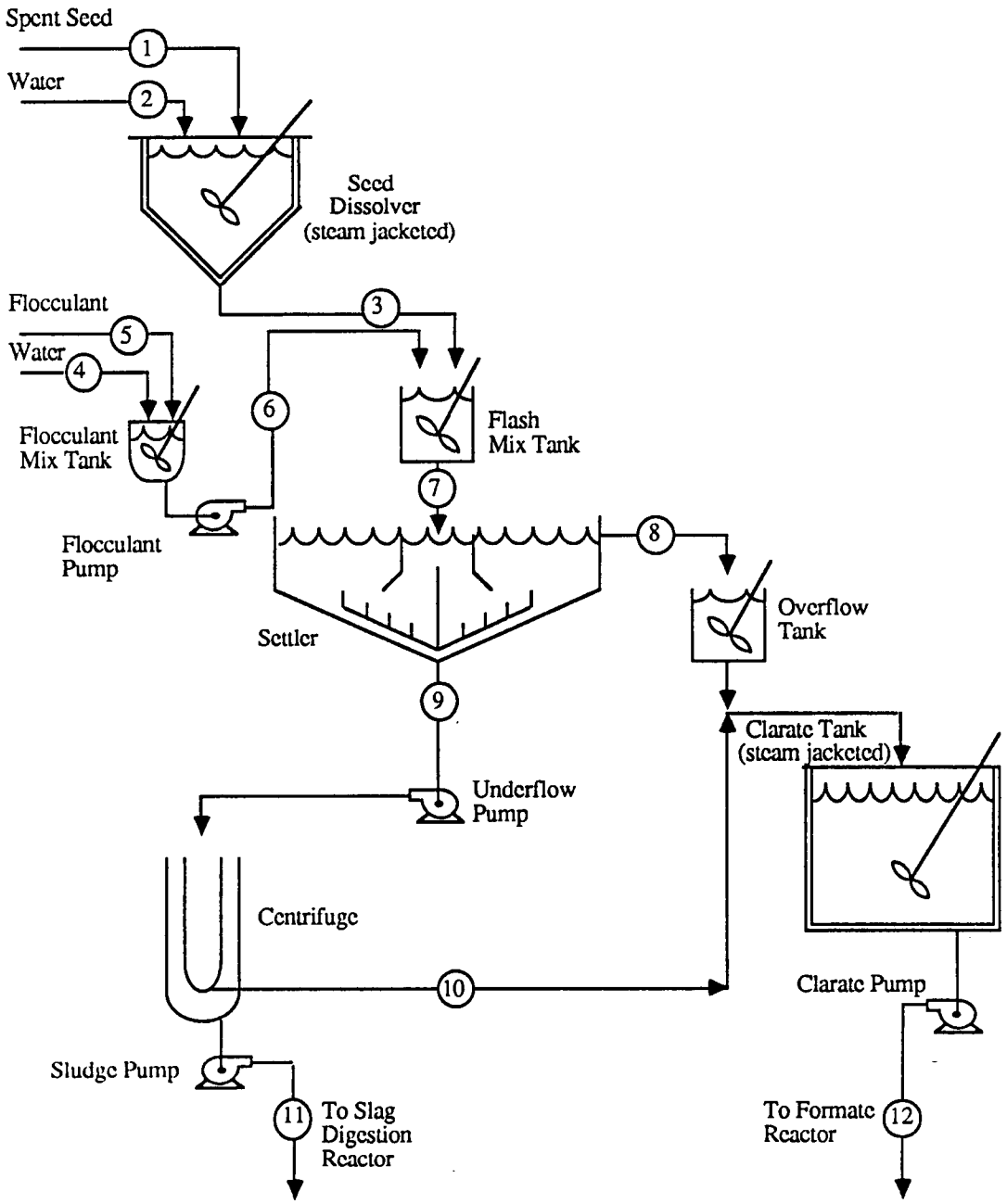

Figure 24. Process Flow Diagram for the Proposed Settler-Centrifuge System

7766 in the form of an emulsion will be added to the slurry. The mixture is then flash mixed at high speed to start the flocculation of insoluble solids. The slurry is then fed to the settling tank. The overflow clear liquid is withdrawn from the top of the tank with flow restricted by a weir. Compaction of the sludge is done by use of a rake at the bottom of the settler. The underflow sludge exits the settler at the bottom with a concentration of approximately 25 percent by weight solids. This underflow is pumped to a centrifuging filter operating continuously. The sludge is further concentrated to approximately 55 percent by weight solids. This removes an additional 70 percent of the soluble liquid contained in the underflow. The clear liquid from the centrifuge is combined with the overflow of the settler to be fed to the formate reactor. The concentrated sludge from the centrifuge is fed to the slag digestion system where it is mixed with slag from the radiant furnace of the MHD system and lime. This mixture of slag material and lime is reacted at elevated temperature to produce KOH by the reaction given in Chapter II.

Choice of a System for Formate Products Solid-Liquid Separation

The choice of a system for the separation of the soluble product stream from the insoluble gypsum containing stream was dictated by preliminary results which indicated that a filter would be adequate to complete the separation. A rotary drum filter was selected for continuous operation. The use of a filter precoat, sold under the tradename Speedex by the Dicalite Corporation, was determined to give the best filtration rate. Body feeds were not considered because of the concern that the formate reaction might be reversible giving the undesirable by-product of calcium formate if the mixture were not separated immediately.

The feed stream is a combination of the formate reactor products and the slag leaching products. The rotary drum filter was designed to have a submergence

of 30 percent with a drum speed of 1 rpm. The use of filter precoats in an amount sufficient to give a 0.5 centimeter thick precoat layer was determined by experimental work to be adequate.

Process Design Basis

The overall mass balance for the solid-liquid separation system is based on an MHD plant capable of producing 100 MW_e, as given in Table XV. The design basis for the overall mass balance was taken from design work done by RCC [2] on a 300 MW_t plant. The basis for the 300 MW_t design was taken by RCC from the operation of the CFFF at Tullahoma, Tennessee. The CFFF is designed to operate at a nominal thermal input of 28 MW_t but normally operates at 18 MW_t. This gives a seeded coal consumption of approximately 0.9 pounds per second. Based on a slag rejection of 60 percent, the seeded coal (88 percent coal, 12 percent K_2SO_4 seed by weight) produces 0.1886 pounds of spent seed per pound of raw coal and corresponding slag production of 0.0268 pounds per pound of raw coal. This leads to a ratio of slag to spent seed of 0.1421 pounds slag per pound of spent seed. Scaling up to 300 MW_t the spent seed production is 8,066 pounds per hour with slag production of 1,146 pounds per hour. Assuming that the spent seed is 85.2 percent soluble K_2SO_4, the amount of soluble potassium sulfate for the 300 MW_t plant is 6,872 pounds per hour. Total production of slag material, including the 1,194 pounds per hour as insoluble spent seed, is 2,334 pounds per hour.

Table XVI gives the material balance for the Settler-Centrifuge system. The stream numbers refer to Figure 24. A block flow diagram of the complete Formate Process is also given in Figure 25. Results of a material balance calculation for the complete Formate Process are given in Table XVII.

Table XV. Design Basis for Proposed Solid-Liquid Separation System.

MHD Plant Size	100 MW_e
Overall MHD Plant Efficiency	33.3% (300 MW_t)
Plant Capacity Factor	0.65 (237.25 days/calendar year)
MHD Plant Life	30 years
Maintenance Cost	4% of equipment costs
Type of Coal	Illinois #6 dried to 2% moisture as fired
Potassium Flow Rate	1% of total primary gas flow
Oxygen Enrichment	46.8 molar % O_2
Stoichiometric Ratio	0.85 (primary)

Table XVI. Summary of Material Balance Calculations for the Spent Seed Solid-Liquid Separation System. (All values in pounds per hour)

Basis: As listed in Table XV.

Stream	K_2SO_4	H_2O	Insolubles	Floc
1	6872	0	1194	0
2	0	47768	0	0
3	6872	47768	1194	0
4	0	11.2	0	0
5	0	0	0	1.12
6	0	11.2	0	1.12
7	6872	47779	1194	1.12
8	6599	45877	6.4	0
9	274	1902	1187	1.12
10	197	1369	5.9	0
11	76	532	1181	1.12
12	6796	47248	12.3	0

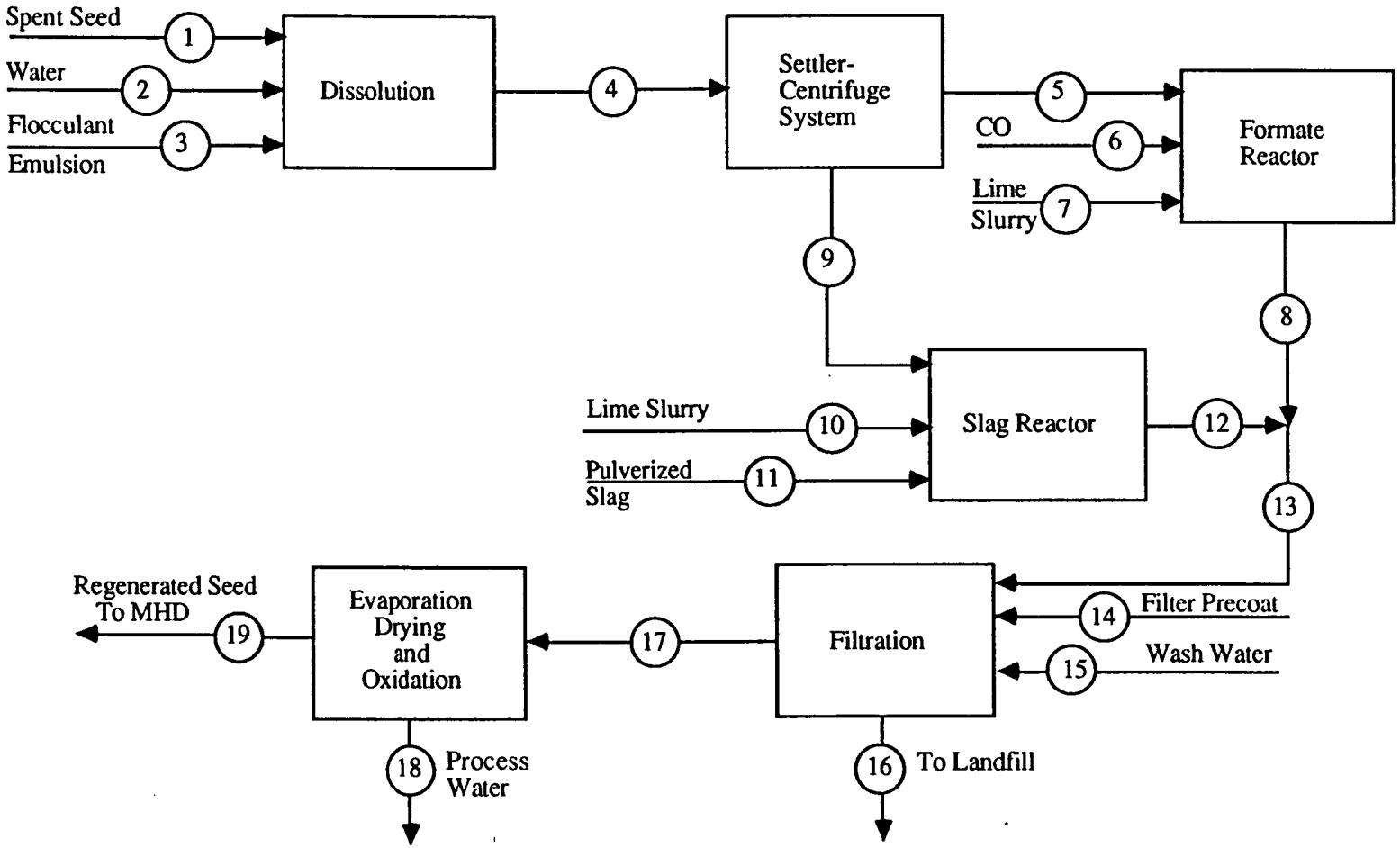

Figure 25. Schematic Block Diagram of the Formate Process

Table XVII. Overall Material Balance for Formate Process.

(All values in pounds per hour.)

Basis: As listed in Table XV.

Stream No.	K_2SO_4	H_2O	Slag	$Ca(OH)_2$	$Ca(COOH)_2$	CO	$CaSO_4$	KCOOH	KOH	K_2CO_3	Floc.	Filter Aid
1	6872	0	1194	0	0	0	0	0	0	0	0	0
2	0	47768	0	0	0	0	0	0	0	0	0	0
3	0	11.2	0	0	0	0	0	0	0	0	1.12	0
4	6872	47779	1194	0	0	0	0	0	0	0	1.12	0
5	6796	47247	12.3	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	4617	0	0	0	0	0	0
7	0	27865	0	3123	0	0	0	0	0	0	0	0
8	136	75112	12.3	0	511	0	5205	6430	0	0	0	0
9	77	532	1182	0	0	0	0	0	0	0	1.12	0
10	0	5262	0	590	0	0	0	0	0	0	0	0

†Continued on next page.

Table XII. (Continued.)

Stream No.	K_2SO_4	H_2O	Slag	$Ca(OH)_2$	$Ca(COOH)_2$	CO	$CaSO_4$	KCOOH	KOH	K_2CO_3	Floc.	Filter Aid
11	0	0	1146	0	0	0	0	0	0	0	0	0
12	77	5794	2128	400	0	0	0	0	402	0	1.12	0
13	213	80906	2140	400	45	0	5205	7032	0	0	1.12	0
14	0	247	0	0	0	0	0	0	0	0	0	24.7
15	0	2832	0	0	0	0	0	0	0	0	0	0
16	8.8	3598	2140	400	45	0	5101	290	0	0	1.12	24.7
17	204	80387	0	0	0	0	104	6742	0	0	0	0
18	0	80387	0	0	0	0	0	0	0	0	0	0
19	204	0	0	0	0	0	104	0	0	5778	0	0

Equipment Sizing

The basis for the sizing of all the proposed major equipment items (i.e. settler, centrifuge, and filter) is the overall area requirement. Table XVIII summarizes the area for each major component. For the settler, the required area will therefore be product of the unit area determined from Chapter VI and the flow rate of solids (insolubles) in tons per day into the system. The only design choice that must be made is whether to use the unit area predicted by the Oltmann construction or the unit area by the Talmadge-Fitch construction. Stevenson [8] reports that the Kynch-based Talmadge-Fitch model tends to underestimate the critical flux and therefore overdesigns the settler. The current model most favored is the Oltmann procedure. While not based on a rigorous theory, the Oltmann construction has been proven in industry to accurately predict settler areas. For this reason, the results obtained from the Oltmann construction were used for design purposes.

For the centrifuge, a generalized approach was taken to determine the volumetric flow rate requirements through the centrifuge. From this and the knowledge of the required residence time for the separation to be completed (based on experimental results), the volume of the centrifuge was specified and thus the equivalent area. Recovery was specified to be 68 percent with a corresponding residence time of 10 minutes at a tangential velocity of 2.13×10^5 cm/s (just as easily, a residence time of 8 minutes at 4.30×10^5 cm/s could have been chosen for the same recovery; however, it can be shown that this option would have resulted in a larger equivalent area).

Table XVIII. Summary of Major Equipment Sizes.

Item	Area (ft^2)
Settler	99.8
Centrifuge	2904.0*
Filter (Formate Products)	410.9

* Represents an equivalent area and not an actual area.

For the Formate Products filter, using equation 31 of Chapter IV, the total area of the rotary drum filter was determined based on the volumetric flow rate through the system. A drum speed of 1 rpm and submergence of 30 percent with a pressure drop of 24 inches of Mercury were taken as design parameters.

Preliminary Economics

Based on the mass balance completed for the overall system, a preliminary cost estimate has been prepared as recommended by the Electric Power Research Institute Technical Assessment Guidelines (EPRI-TAG) [20]. All costs are reported in early 1988 dollars. Major equipment items except for the centrifuging filter were costed by RCC as part of DOE contract no. DE-AC22-87PC79671 [2]. The estimated cost of the centrifuging filter was taken from Backhurst and Harker [19]. Table XIX gives the cost breakdown for each item of equipment for the solid-liquid separation system. All items are priced delivered and in some cases set-up. The installation cost was taken to be 62 percent of the purchased equipment cost and level ratioed for each item. Indirect construction was likewise level ratioed at 58 percent of the equipment and installation costs. Because all of the equipment items involve established technology, a process contingency of zero was assumed. A project contingency of 15 percent was taken due to the preliminary nature of the design. An engineering fee of 10 percent of the total equipment requirement (including installation, indirect construction, and contingency) was added to arrive at the total capital cost of the solid-liquid separation system.

Table XX gives a summary of the total capital cost of the solid-liquid separation system along with the remainder of the Formate Process. Escalation and Allowance for Funds During Construction were calculated using EPRI-TAG [20] based on an idealized construction time of 3 years. A royalty allowance of 1.02 dollars per kilowatt of electricity produced was assumed. Preparation costs including costs of training personnel, lost income during start-up, and related activities were computed as 2 percent of the total capital cost. Initial chemicals and catalyst were calculate based on a 60 day inventory.

Table XIX. Capital Cost Estimate for 300 MW_t Formate Plant Solid-Liquid Separation System.

(All values in thousands of 1988 dollars.)

Item	Material Cost	Installation	Construction	Contigency	Total
Spent Seed Settler-Centrifuge System					
Major Items					
Seed Dissolver	3.820	2.368	3.589	1.467	11.244
Flocculant Tank	0.840	0.521	0.789	0.323	2.473
Flash Mix Tank	3.400	2.108	3.195	1.305	10.008
Settler	22.000	13.640	20.671	8.447	64.758
Centrifuge	17.000	10.540	15.973	6.500	50.013
Overflow Tank	3.400	2.108	3.195	1.305	10.008
Clarate Tank	20.000	12.400	18.792	7.679	58.871
Subtotal-Major Items	70.460	43.685	66.204	27.026	207.447
Minor Items					
Flocculant Pump	0.900	0.558	0.846	0.346	2.649
Underflow Pump	2.200	1.364	2.067	0.845	6.476
Sludge Pump	1.200	0.744	1.128	0.461	3.532
Clarate Pump	2.400	1.488	2.255	0.921	7.064
Seed Dissolver Mixer	5.600	3.462	5.262	2.150	16.484
Flash Tank Mixer	0.230	0.143	0.216	0.088	0.677
Flocculant Tank Mixer	0.500	0.310	0.470	0.192	1.472
Overflow Tank Mixer	0.500	0.310	0.470	0.192	1.472
Clarate Tank Mixer	9.000	5.580	8.456	3.455	26.492
Subtotal-Minor Items	22.530	13.969	21.170	8.650	66.318

Table XIX. (Continued.)

Item	Material Cost	Installation	Construction	Contigency	Total
Formate Products Filtration System					
Major Items					
Reactor Product Mix Tank*	3.400	2.108	3.195	1.305	10.008
Reactor Product Filter	380.000	235.600	357.048	145.897	1118.545
Wash Tank	1.300	0.806	1.221	0.499	3.827
Subtotal-Major Items	384.700	238.514	361.464	147.701	1132.380
Minor Items					
Reactor Product Mix Pump	3.000	1.860	2.819	1.152	8.831
Reactor Product Mixer	2.800	1.736	2.631	1.075	8.242
KCOOH Filtrate Pump	5.000	3.100	4.698	1.920	14.728
Subtotal-Minor Items	10.800	6.696	10.148	4.147	31.791
TOTALS	488.490	302.864	458.986	187.524	1437.936
Engineering Fee		143.794			143.794
TOTAL CAPITAL COST					1581.730

* Includes Filter Aid, Mixer, and Pump.

Table XX. Total Capital Requirement for 300 MW_t Formate Plant.

(All values in thousands of 1988 dollars.)

Line Item	Cost
Total Capital Requirement	
Proposed SLS System	1581.730
Formate Process(minus SLS) [2]	19839.829
Subtotal	21421.559
Escalation	1328.137
Allowance for Funds During Construction(AFDC)	2527.744
Royalty Allowance	102.000
Preparation Costs	428.431
Initial Chemicals and Catalyst	154.041
TOTAL CAPITAL COST	25961.942

A breakdown of the consumables cost is given in Table XXI. As can be seen the major expenditures are made in the areas of plant power and low pressure steam. Both the flocculant and the filter aid (diatomaceous earth) are relatively inexpensive when compared with other expenditures.

A summary of the operating and maintenance costs for the solid liquid separation system is given in Table XXII. The operating and maintenance costs for the Formate Process are also included. Operating labor was calculated based on a total manpower requirement of the solid-liquid separation system of 1 equivalent manpower (three men on three 8-hour shifts). For the complete Formate Process, an additional 2 1/3 manpower were required. Maintenance was computed as 4 percent of the total equipment investment. Of this, 40 percent was assumed to be materials and 60 percent labor. Administrative and support labor were calculated as 30 percent of the total operation and maintenance labor.

Table XXI. Summary of Consumables Costs for Proposed Solid-Liquid Separation System.

(Unless otherwise specified, all costs in thousands of 1988 dollars.)

Item	Quantity		Unit Cost	Initial Cost	Daily Cost	Annual Cost
	Initial	Daily				
Cooling Water (/1000 gal)		148.0	0.71		0.105	24.930
Flocculant (/pound)	1626.	27.1	2.50	4.065	0.068	16.133
Diatomaceous Earth (/pound)	32472.	541.2	0.124	4.027	0.067	15.922
Plant Power (/KWHR)		6908.0	0.05359		0.370	87.830
L.P. Steam (/1000 pound)		121.1	3.59		0.435	103.144
TOTALS				8.092	1.045	247.959

Table XXII. Summary of First Year Operating and Maintenance Costs for 300 MW_t Formate Plant with Proposed Solid-Liquid Separation System. (All values in thousands of 1988 dollars.)

Line Item	Cost
Operation and Maintenance	
Proposed SLS System	
Operating Labor	205.860
Maintenance Labor	7.816
Maintenance Material	11.724
Administrative and Support Labor	11.724
Subtotal-Proposed SLS System	289.503
Formate Process(minus SLS) [2]	864.588
TOTAL O&M	1154.091
Consumables	
Proposed SLS System	247.959
Formate Process(minus SLS) [2]	5322.976
TOTAL CONSUMABLES	5570.935

Economic Evaluation

Based on the preliminary economics presented, the proposed SLS system represents approximately 7.4 percent of the $26.0 million total capital cost of the Formate Process. The proposed Formate product filter system is the most costly equipment system representing nearly 75 percent of SLS expenditures. The proposed SLS system also accounts for 7.8 percent of the first year Operating and Maintenance and Consumables costs for the Formate Process, with the majority of the consumable for the SLS system being steam and electricity, as expected. The use of additives such as flocculants and diatomaceous earth adds very little to the overall cost of the SLS consumables. Therefore, the utilization of such additives will likely be economically advantageous.

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

From the solid-liquid separation study carried out on the Formate Process-based Seed Reprocessing option in this thesis, the following conclusions can be drawn:

- The separation of soluble potassium sulfate contained in MHD spent seed material is best accomplished using a settler-centrifuge system.
- Flocculation of the small insolubles in the spent seed is necessary to shorten the required settling time, thus reducing the area of the settler. The anionic flocculant Nalco 7766 in doses of 20 ppm is found to be the most effective among the ones that were tried.
- A filtering centrifuge is the preferred method for dewatering of the underflow (sludge) from a settler. Experimental evaluation shows the centrifuge to perform much better than a standard filter.
- A rotary drum filter, with use of a precoat material, is found to be an efficient means of separation of the insoluble gypsum and slag like material from the Formate containing solution. A Perlite type compound, manufactured by the Dicalite Corporation under the tradename of Speedex, is found to be the most effective precoat material of those tested.
- An amount of wash water equivalent to 3.5 percent of the slurry volume at the Formate products filter is sufficient to recover over 99 percent of the soluble fraction (containing potassium) of the Formate product stream contained in the filter cake.
- Preliminary economic evaluation of the proposed solid-liquid separation sys-

tem (including the settler-centrifuge for spent seed separation and the filter for Formate product separation) indicates that the proposed system represents a considerable portion of the cost of the Formate Process-based Seed Reprocessing Option (approximately 8 percent of the capital and operating and maintenance costs) . Thus, careful consideration must be given to this important system to reduce the overall cost of seed recovery and regeneration.

Recommendations

Obviously, more work will need to be done on a larger scale to confirm the results of the bench scale experiments presented here. Based on the current MHD program planned by DOE, a proposed second phase will evaluate one option for seed reprocessing at the pilot plant scale. If the Formate Process is selected for Phase II consideration, a larger data base on the various solid-liquid separation schemes will be obtained in pilot plant scale. In particular, the following areas need further consideration during the Phase II activities:

- Steady state operation of the settler will be necessary in order to determine its effective operation range. Bench scale studies of agitated systems (to simulate an actual settler with operating rake system) should offer valuable insight into the operation of a larger scale unit.
- A more detailed study of flocculants should be conducted to determine the best flocculant for larger scale operations based on performance and economics.
- Operation of a pilot plant scale drum filter will be necessary to determine the best operating cycle, drum submergence, and filter precoat thickness for the Formate/slag leaching product mixture. A suitable media for the drum filter will also be determined during this testing.

LIST OF REFERENCES

LIST OF REFERENCES

1. Jackson, D.M., "Evaluation of Seed Regeneration Processes for Coal-Fired MHD Power Plants," FE-1760-36, a report prepared by the University of Tennessee Space Institute for DOE under Contract No. DE-ACC02-79ET10815, 1985.

2. Sheth, A.C. *et.al*, "MHD Seed Recovery and Regeneration Based on the Formate Process," Phase I Final Report, a report prepared by the University of Tennessee Space Institute and Resources Conservation Co. for DOE/PETC under Contract No. DE-AC22-87PC79671, October 1988.

3. "Exxon Catalytic Coal Gasification Process: Predevelopment Program," Annual Report, July 1976-June 1977, FE-2369-20, Exxon Research and Engineering Company, Baytown, Texas, January, 1978.

4. Internal Memorandum from Holt, J.K., "Potassium Recovery through Slag Leaching," University of Tennessee Space Institute, Tullahoma, Tennessee, April 1986.

5. A private communication with Wilson, G.L., Resources Conservation Co., Bellevue, Washington 1988.

6. Templemeyer, K., L. Shen, J. Brewer, and M. Beaton, "Investigation of the potential of Acid Washing of Coal Ash to Enhance Potassium Recovery in a High Ash carryover Direct Coal-Fired MHD System," Conference on High Temperature Sciences Related to Open-Cycle, Coal-Fired MHD System, Argonne National Laboratory, Argonne, Illinois, April 4-6, 1977, pp. 254-259.

7. Patil, A.T., "Development of Potassium Recovery System for MHD-Spent Seed Containing Materials," master's thesis, The University of Tennessee, Knoxville, December 1988.

8. Purchas, D.B. (*ed.*), "Solid/Liquid Separation Equipment Scale-up," Uplands Press Ltd., 39-67,81-153(1977).

9. Sheth, A.C., "Bench Scale Settling and Filtration Studies on CCG Char," a project report, Proprietary Report No. 5360-115tf, Exxon Research and Engineering Company, Baytown, Texas, August 1981.

10. Lewis, W.K., (untitled), *Chem. and Met. Eng.*, **27**(12), 594(1922).

11. Ambler, C.M., "Evaluation of Centrifuge Performance", *Chem. Eng. Progress*, **48**, 150(1952).

12. Frampton, G.A., "Evaluating the Performance of Industrial Centrifuges," *Chem. and Process Eng.*, pp. 402, August 1963.

13. Tiller, F.M. *et al.*, "Theory and Practice of Solid-Liquid Separation," University of Houston, Texas 1975.

20. Nalco 7766 is a product manufactured and sold by the Polymers Division of the Nalco Corporation.

15. A private communication with Patil, A.T., University of Tennessee Space Institute, Tullahoma, Tennessee, 1988.

16. Speedex is a product manufactured and sold by the Grefco Division of the Dicalite Corporation.

17. Perry, Robert H. and C.H. Chilton, Chemical Engineer's Handbook, 5th ed., McGraw-Hill Book Company, New York, 1973.

18. A private conversation with Solomon, R.L., Resources Conservation Co., Bellevue, Washington, 1988.

19. Backhurst, J.R. and J.H. Harker, "Process Plant Design," American Elsevier Publishing Company, Inc., New York, 1973.

20. "Electric Power Research Institute Technical Assessment Guidelines(TAG)," Volume 1: Electricity Supply, EPRI reference number P-4463s-SR, prepared by Technology Evaluation Section, Special Report December 1986.

VITA

Darryll Glen Rasnake was born in Tazwell County, Virginia in 1965. He attended the Monroe County, Tennessee school system until his graduation from Madisonville High School in 1983. The following fall he entered Tennessee Technological University and received a Bachelor of Science, cum laude, in Chemical Engineering in June of 1987. In the fall of 1987, he received a graduate research assistantship at the University of Tennessee Space Institute (UTSI) in the Energy Conversion Program. He also received distinction as the first Dean's Scholar at UTSI. He received a Master of Science in Chemical Engineering from UTSI in May, 1989.