27
7/25/82 T.S.

ORNL/TM-6647/V2

OAK
RIDGE
NATIONAL
LABORATORY

UNION
CARBIDE

MASTER

**Advanced Technology Section
Semiannual Progress Report for
the Period April 1, 1978, to
September 30, 1978 Volume 2:
Engineering Science Programs**

J. S. Watson
S. D. Clinton

OPERATED BY
UNION CARBIDE CORPORATION
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes—Printed Copy: A06 Microfiche A01

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

ADVANCED TECHNOLOGY SECTION SEMIANNUAL PROGRESS REPORT

FOR THE PERIOD APRIL 1, 1978, TO SEPTEMBER 30, 1978

VOLUME 2: ENGINEERING SCIENCE PROGRAMS

Compiled by:

J. S. Watson
S. D. Clinton

Date Published: July 1980

NOTICE This document contains information of a preliminary nature.
It is subject to revision or correction and therefore does not represent a
final report.

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
DEPARTMENT OF ENERGY

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

CONTENTS

	<u>Page</u>
SUMMARY	v
I. INTRODUCTION.	1
2. CHEMICAL ENGINEERING RESEARCH	2
2.1 Continuous Chromatography.	2
2.2 Fundamental Agglomeration Studies in Heavy Organic Media	7
2.2.1 Introduction.	7
2.2.2 Theory.	9
2.2.3 Procedure for measuring the stability of particles inorganic liquids	12
2.2.4 Procedure for measuring zeta potentials	13
2.2.5 Experimental results.	17
2.2.6 Zeta potential measurements	26
2.3 Removal of Solids in a Granular Filter	30
2.4 High-Temperature Slagging.	37
2.4.1 Introduction.	37
2.4.2 Program status.	41
2.5 References for Section 2	41
3. HYDROGEN ISOTOPE TECHNOLOGY	43
3.1 Cryosorption Vacuum Pumping.	43
3.1.1 Survey of sorbents and temperature for hydrogen pumping	44
3.1.2 Compound pump development for hydrogen-helium mixtures.	54
3.2 Tritium Recovery from Yttrium Getters.	64
3.2.1 Experimental apparatus.	65
3.2.2 Results and discussion.	65
3.2.3 Program status.	65
3.3 Tritium Sorption from Liquid Metals.	67
3.3.1 Experimental apparatus.	67
3.3.2 Program status.	69
3.4 Hydrogen Isotope Separation in Aqueous Systems Using Bipolar Electrolysis with Hydrogen-Permeable Electrodes.	69
3.4.1 Background.	70
3.4.2 Estimations of the maximum current densities from permeation rates of hydrogen and deuterium through 75% palladium--25% silver	72
3.4.3 Analysis of experimental data	74
3.4.4 Conclusions	90
3.5 References for Section 3	94

	<u>Page</u>
4. RESOURCE RECOVERY	96
4.1 Recovery of Resource Materials from Coal Ashes	96
4.2 References for Section 4	100

SUMMARY

Chemical Engineering Research

Studies of continuous chromatography investigated the separation of iron and aluminum, the two major metal components obtained from acid leaching of coal ash. Acid nitrate solutions ($\text{pH} = 1.4$) simulating diluted leach liquors were loaded on a column of Dowex 50W-X8 and eluted with a solution containing $0.5 \text{ M } (\text{NH}_4)_2\text{SO}_4$ and $0.025 \text{ M } \text{H}_2\text{SO}_4$. This eluted the iron in one portion of the continuous chromatograph. In the portion of the chromatograph that followed, the eluent was changed to $1 \text{ M } (\text{NH}_4)_2\text{SO}_4$ with $0.025 \text{ M } \text{H}_2\text{SO}_4$, and the aluminum was removed.

Studies of agglomeration processes included measurements of the particle size and zeta potential of solids in coal-derived liquids. Similar measurements were made of carbon black in cyclohexane, a well-characterized system, to test the experimental technique.

A new study of filtration in deep granular beds in the presence of electric fields produced promising results indicating that this may be an effective and practical polishing technique for removing the ultrafine ($<1\text{-mm-diam}$) particles from coal-derived liquids. Simulated studies using 1-mm particles in cyclohexane showed that particle removal efficiencies approaching 100% can be achieved. The removal rate increases with increasing electric field strength and with decreasing liquid velocities. The pressure drop through the beds is very small, and the electric power requirements are essentially negligible.

Another new study began investigating the use of high-temperature slagging processes for the purification of recycled metals. A preliminary survey identified the removal of copper from recycled iron-based alloys

as a particularly important problem, and contactor development studies were initiated using mercury and water to simulate the fluids of interest.

Hydrogen Isotope Technology

Hydrogen pumping speeds on panels of molecular sieve types 5A and Na-Y were compared for a variety of sieve (and chevron) temperatures between 10 and 30 K. Although pumping speeds declined with time, probably because of the slow diffusion of hydrogen from the surface of the sieve crystals into the internal regions, the different sieve materials and operating conditions could be compared using time-averaged pump speeds. The (average) pumping speeds declined with increasing temperature. Under some conditions, the Na-Y sieve performed much better than the 5A sieve. Studies of the effect of small concentrations (~4%) of hydrogen on helium pumping indicate that compound cryopumps in fusion reactors will not have to provide complete screening of hydrogen from helium panels. The concentrations of hydrogen did not lower effective helium pumping speeds or shorten the helium operating period between instabilities.

Studies of tritium recovery from blankets of liquid lithium focused on design and construction of a flowing-lithium test system and on ultimate removal of tritium from yttrium sorbents. At 505°C, tritium release from yttrium behaves as a diffusion-controlled process, but the release rates are very low. Apparently, higher temperatures will be required for effective sorbent regeneration.

An innovative technique for separating hydrogen isotopes by using bipolar electrolysis with permeable electrodes was analyzed to determine its potential usefulness in multistage separation. The technique has been studied experimentally in the ORNL Solid State Division, and the

results of the recent analysis were compared with Solid State's data. Multistage units that incorporate this technique will behave according to McCabe-Thiele systems, and relatively simple analyses can be used. High degrees of separation should be possible; however, this was not demonstrated in previous experiments because the ratio of the liquid flow rate to electric current was too high.

Resource Recovery

The Calsinter process, originally designed to use CaSO_4 and CaCO_3 as sintering reagents, was shown to be effective when flue-gas desulfurization sludge (FGDS) is used as one of the reagents. Studies of the behavior of trace metals in fly-ash processing were initiated; these trace components may be especially important if they are toxic and affect ash disposal. Initial studies of direct-leach processing for coal gasification ash indicate that metal recovery may be less difficult and expensive from these materials than from fly ash. Gasification ashes are not fired to the high temperatures that fly ash is and are more reactive.

1. INTRODUCTION

The Engineering Science Program in the Advanced Technology Section consists of three parts: (1) Chemical Engineering Research, (2) Hydrogen Isotope Technology, and (3) Resource Recovery. The Chemical Engineering Research studies and the Resource Recovery studies are funded by the DOE/Office of Basic Energy Sciences and are relatively fundamental. The Hydrogen Isotope Technology studies include fundamental studies funded by the DOE/Office of Basic Energy Sciences of techniques for recovering tritium from the blanket of fusion reactors, applied studies funded by the DOE/Office of Fusion Energy on vacuum pumping in fusion reactors, and an analysis funded by the DOE/Office of Waste Management of hydrogen isotope separation by bipolar electrolysis with permeable membranes.

2. CHEMICAL ENGINEERING RESEARCH

The Chemical Engineering Research program includes fundamental studies of chemical engineering problems that are important to energy development. These studies are funded by the DOE/Office of Basic Energy Sciences and are important to fossil fuel development, nuclear fuel processing, and a variety of separation processes.

2.1 Continuous Chromatography

R. M. Canon

Investigations during this period concentrated on the separation of iron and aluminum from an acid solution. The resource recovery effort produces acid liquors (from the leaching of coal ash) containing significant amounts of iron and aluminum as well as smaller quantities of many other metals. Efficient separation of these metals has not been demonstrated by other methods; therefore, continuous chromatography is being examined for this application.

The literature gives methods for the separation of a large number of these metals via conventional ion exchange. However, these are analytical methods that are suitable for small quantities but not for preparative scale work. They use many eluents, including HCl, H₂SO₄, and methanol, in various concentrations and combinations. The resin-specific volume changes occurring with these eluents prohibit their use in the continuous chromatograph. Therefore, a new system was sought to separate these metals in an acid solution. Because aluminum and iron are the major components, the development of methods to separate these metals was given priority.

Simulated liquors containing iron and aluminum nitrates were used for the feed solutions. Dowex 50W-X8 cation exchange resin, the same resin used previously for the cobalt-nickel-copper system, was used for all tests. Because the metals will not load from the high-acid liquor, neutralization (or evaporation) to a pH of about 1.4 is required before feeding to the column. Solutions of $(\text{NH}_4)_2\text{SO}_4$ and H_2SO_4 were examined for use as eluents, and distribution coefficients were measured. Figure 2.1 shows the distribution coefficients of aluminum and iron in solution with 0.025 M H_2SO_4 and various concentrations of $(\text{NH}_4)_2\text{SO}_4$. The coefficients were determined from column measurements on a conventional 0.50-in.-diam column. The distribution coefficient was calculated from

$$K = \frac{V_R - V_0}{V_T - V_0}, \quad (1)$$

where

V_R = volume of eluent used to elute the solute at peak concentration,

V_0 = void volume of the column,

V_T = total volume of the column.

In several experiments with a single eluent, relatively poor results were obtained. With low concentrations of $(\text{NH}_4)_2\text{SO}_4$ in the eluent, dilution of aluminum was high; higher $(\text{NH}_4)_2\text{SO}_4$ concentrations (>0.25 M) would not give separation. Consequently, a gradient elution was used. The method of control for this operation has been described previously.¹

Figure 2.2 shows the separation for a feed containing 4.0 g of iron per liter and 7.0 g of aluminum per liter. Angular displacements were measured from the feed point. With the feed point at 0° , the area

ORNL DWG 78-17859

Fig. 2.1. Distribution coefficients of aluminum and iron in 0.25 M H_2SO_4 as a function of $(\text{NH}_4)_2\text{SO}_4$ concentration.

Fig. 2.2. Continuous separation of iron and aluminum using gradient elution chromatography. The vertical line represents the interface of the two eluents.

receiving 0.5 M $(\text{NH}_4)_2\text{SO}_4$ and 0.025 M H_2SO_4 extended from 303° to 123°; the remainder received 1.0 M $(\text{NH}_4)_2\text{SO}_4$ and 0.025 M H_2SO_4 . The rotation rate was 210°/h; the feed rate was 4.05 cm³/min; and the superficial eluent velocity was 2.29 cm/min. These conditions were chosen to enable the iron to elute simultaneously with the arrival of the second (higher-concentration) eluent. The second eluent quickly eluted the aluminum, compressed the band, and significantly reduced the amount of dilution. Table 2.1 compares isocratic and gradient elution. Dilution (concentration in the feed/concentration in the eluted band) was reduced spectacularly for aluminum and significantly for iron. Recovery (grams of metal fed per minute/grams of metal recovered in the product band per minute) was also significantly improved, and cross contamination was reduced slightly. Cross contamination refers to the concentration of the contaminant (minor) metal in the product metal after the product stream is reduced to the metal. Thus, the aluminum in the product obtained in run FEA-18 would contain 0.66% iron by weight.

Table 2.1. Comparison of isocratic and gradient elution results for iron and aluminum

Run Number	Conditions	Dilution		Recovery (%)		Cross contamination (%)	
		Fe	Al	Fe	Al	Al in Fe	Fe in Al
FEA-1	Isocratic	19.3	51.5	80	78	0.069	1.00
FEA-18	Gradient	7.4	8.5	92	98	0.029	0.66

These results indicate that aluminum and iron can be separated using continuous ion-exchange methods with gradient elution techniques. Investigations of this system are continuing, and the system will be expanded to include titanium, manganese, and other metals. However, the process may prove most useful in separating or isolating the many trace metals found in the leach liquors, especially those metals known to be hazardous. Additional studies will be required to further improve the separation of the major components.

2.2 Fundamental Agglomeration Studies in Heavy Organic Media

B. R. Rodgers and J. D. Hewitt

2.2.1 Introduction

The tendency for particles to agglomerate and precipitate, or to disperse and stabilize, is characterized by a number of physical parameters,²⁻⁴ the most obvious of which are size and density relative to the suspending matrix. Generally, colloidal dispersions are defined as dispersed particles with diameters of less than 1 μm ; this artificial limit corresponds roughly to the maximum possible size for a particle that will stay in suspension for a reasonable time. In heavy organic systems, such as coal liquefaction products, unconverted coal and mineral matter may be present both as a suspension (particles $>1 \mu\text{m}$) and as a colloidal dispersion (particles $<1 \mu\text{m}$). The particles in suspension are not difficult to remove by conventional techniques; however, this is not true of the particles in the colloidal dispersion, which often constitute up to 50% by volume of the total particle mass⁵ and which must be removed to meet stringent Environmental Protection Agency specifications.

Agglomeration followed by sedimentation is an effective separations technique for coal-derived materials,⁶ but little is known about the mechanism of agglomeration.

The properties of colloidal dispersions may be altered by effecting a change in particle size distribution, and hence superficial interfacial area, or by changing the nature of the interfacial forces by using electrolytes or surface-active agents. Even though the agglomerated condition represents the lowest thermodynamic energy state, an energy barrier exists that prevents particle adhesion. Thus the rate of agglomeration depends on the collision frequency of the colloidal particles and the surface energy relative to the energy barrier. Because colloidal particles undergo Brownian motion, the collision frequency can be increased by raising the solution temperature. However, the energy barrier that prevents the close approach of particles must also be lowered or little agglomeration will occur. Verwey and Overbeek² showed that energy barriers can be caused by overlapping double layers; the layers interact to increase the free energy of the system and thereby lead to a potential energy of repulsion. The stability of an electrolyte suspension is determined by the balance between these repulsive forces and the attractive Van der Waals forces. The zeta potential, a measure of the repulsive strength of the outer electric double layer, can often be related to the agglomerating tendency of the dispersion.

Kitahara,^{3,7} among others, applied the above theory to nonaqueous (low-electrolyte) systems. This report applies the theory to coal-derived liquids and shows that significant zeta potentials do indeed exist for particles in the liquefaction product. Further experimentation is necessary

to relate this parameter to agglomeration, and thus to separation, of solids from coal liquids.

2.2.2 Theory

The principal theory describing electric double layers was formulated independently by Derjaguin and Landau⁸ and by Verwey and Overbeek² during the forties, and is referred to as the DLVO theory. This theory is generally accepted as the basic theory regarding stability of lyophobic colloids. According to the DLVO theory, the interaction between colloidal particles is controlled by electrostatic repulsion caused by the double layer and attraction caused by the Van der Waals forces. The theory, however, does not adequately describe the stability of polymer and poly-electrolyte dispersions or the effect of very weak electrolyte solutions on lyophilic systems. Nevertheless, significant zeta potentials have been measured for weak electrolyte solutions such as carbon black in benzene,⁹ heptane,¹⁰ and toluene¹¹ and iron and alumina in xylene.¹² Some conductivity was imparted to these solutions by the addition of organic soluble dissolution compounds such as calcium oleate, Aerosol OT (AOT), and calcium diisopropyl salicylate; no zeta potential was measured in the absence of electrolyte.

In the last report in this series, the basic equations of electrokinetics were developed from the arbitrary element balance shown in Fig. 2.3. The general double-layer equation was shown to be

$$\nabla \cdot \underline{\tau} = \rho_c \underline{E} ,$$

where

ARBITRARY VOLUME FORCE BALANCE OF A PARTICLE MOVING THROUGH A STATIONARY
DIELECTRIC MEDIUM UNDER THE INFLUENCE OF AN ELECTRIC FIELD

Fig. 2.3. The electric double layer for a particle with a radius $\gg$ the double-layer thickness.

$\underline{\tau}$ = viscous tensor, kg/m·s,

ρ_c = charge density, C/m³,

$\underline{E}$ = electric field, V/m.

With the use of Poisson's equation,

$$\nabla^2 V_{12} = - \frac{\rho_c}{\epsilon},$$

where

V_{12} = potential, V,

ϵ = permittivity, s²/m³,

the charge density was eliminated to give

$$\frac{\mu}{E} d^2 v_x = \epsilon d^2 V_{12},$$

where

ϵ = viscosity, P,

v_x = velocity in x direction, m.

Integration of this equation gives the standard zeta potential equation for electrophoresis,

$$V_{12} = \frac{\mu v_x}{\epsilon E} \equiv \zeta \text{ (zeta potential)},$$

where the boundary conditions

$$\left. \frac{dv_x}{dy} \right|_{\infty} = \left. \frac{dV_{12}}{dy} \right|_{\infty} = \left. v_x \right|_{\infty} = \left. V_{12} \right|_{\infty} = 0$$

were used to evaluate the integration constants.

2.2.3 Procedure for measuring the stability of particles in organic liquids

The equipment used included a Perkin-Elmer spectrophotometer Hitachi 200-0162 and a Perkin-Elmer recorder Hitachi 200-6260, the two of which operate as a system. With relatively clear solutions, silica spectrophotometer cells manufactured by VWR Scientific, Inc., were used; these rectangular cells have teflon stoppers and a 10-mm light path. With turbid or semitransparent liquids, a semimicro cell with fitted teflon cover was used. As received, these cells had an internal width of 2 mm and a 10-mm light path length; however, the unpolished sides of the semimicro cells were polished, thereby allowing a 2-mm path length. Solutions of varying concentrations of particles in liquids were carefully prepared gravimetrically. The particles were dispersed in an ultrasonic bath for 30 min before insertion in the spectrophotometer. Thirty minutes was also allowed for the spectrophotometer to warm up before starting, and both reference (suspending liquid) and blank (water) solutions were prepared using matched spectrophotometer cells. The spectrophotometer was calibrated using the following procedure:

1. Select the percent T (transmittance) mode.
2. Set slit control to the desired width (nm), approaching setting from a larger value.
3. Set response time and select the appropriate lamp for the type of solution being studied.
4. If recording on chart, set recorder scan-speed selector as required. Set spectrophotometer scan speed if needed.
5. Use wavelength control to set wavelength (higher wavelength if scanning), approaching setting from the higher wavelength direction.

6. Set decimal point selector to percent T-ABS.
7. Insert zero shutter in the sample cell holder. Close sample compartment cover. Adjust 00.0% T with the 0% T control until display balances between t and -00.0.
8. Remove zero shutter, position sample reference and sample blank spectrophotometer cells, and close sample compartment cover. Set 100.0% T with 100% T/O ABS control.
9. If recording on chart, set photometric range and position pen with zero suppression control if necessary.
10. Remove sample blank and substitute first sample to be measured.
11. Read sample value on Digital Display.

In general, the suspending liquid was used as reference (standard), the wavelength varied from 500 to 850 nm, the slit width was 2.0 mm, fast response was best, a 30-mm/min chart speed was the most appropriate, and the W-lamp was required.

2.2.4 Procedure for measuring zeta potentials

Liquefied coal was opaque when the film thickness was greater than 100 μm . To obtain sufficient transparency for microelectrophoresis, a special apparatus had to be constructed. It contained a thin rectangular cell providing a film thickness of $\sim 100 \mu\text{m}$. This cell, which is discussed in previous semiannuals, is shown as Cell B in Fig. 2.4. Platinum electrodes were sputter etched onto the flat glass surface, and the thin capillary groove was diamond lapped onto the matching surface before the "sandwich slide" was cemented with epoxy. In heavy organic systems such as these, platinum had no tendency to produce gassing and thus was an obvious choice for electrode material. The sandwich cell was connected

ORNL DWG 79-7617R2

Fig. 2.4. Microelectrophoresis slides.

to a model D6 Oregon Electronics Regulated Power Voltage Supply and to the stage of a Series 10 Microstar Laboratory Microscope. Observations were made at magnifications of 40X and 100X. Higher magnifications would have been desirable for the smaller particles, but the focal length of the microscope system was too short at higher magnifications to be used with the sandwich slide system.

All velocities were determined using a calibrated eyepiece and a stopwatch. Care was exercised to avoid liquid convection, which occurred at high electric fields, and polarization of electrodes, which occurred after the voltage was imposed for too long. The use of alternating electrode polarity and short time measurements minimized these effects. Because of the difficulty of focusing at an exact level and because the wall effects of this thin film slide are unknown, previous results obtained are considered qualitative and should be used only for comparison within the series.

To obtain quantitative measurements, a 1-mm-thick cell with a parallel electric field, Cell A of Fig. 2.4, was constructed. This cell was used to obtain a precise measurement of the level of zero electroosmotic velocity by the Thompson method given in ref. 13. Because of the blackness of the coal liquids, measurements must be limited to only the oils or the mixtures of oils and resins having low (<1%) concentrations of solids, asphaltenes, or preasphaltenes. The procedure for determining electrophoretic mobility was similar to that described previously except for the level determination.

To cross-check the measurements made with the flat electrophoresis cell (Cell B), a commercial apparatus marketed by Zeta Meter, Inc., was employed with a glass-teflon cell. A schematic of the ZM-77 measuring cell is shown in Fig. 2.5.

Fig. 2.5. Zeta Meter cell.

2.2.5 Experimental results

Stability of particles in organic liquids. Theoretically, zeta potential is related to particle stability in liquids. Settling rate is also related to stability, and because this rate determines the ease of separation of the two phases, it is one of the most important properties to predict. One could argue from these facts that zeta potential should be related to settling rate; however, it is not so simple. Other very important considerations are

1. Particle size and density relative to the liquid. Larger particles are easier to stabilize by charge; smaller particles are more resistant to settling.
2. Particle drag. Particles that associate or have odd shapes do not settle as rapidly as do spheres and thus have a smaller effective diameter for Stokes settling. Pointed particles could have a higher-than-average charge per unit area at the edges, which would offset dispersion.
3. Hindered settling. At higher concentrations, particle-particle interactions become important. Such interactions can result in the limiting case in which liquid is squeezed upward through a packed bed of solids.

Because of the above, one would expect the relationship between zeta potential and settling rate to be complicated. However, with care, it should be possible to define a qualitative relationship indicating degrees of difficulty. In these experiments, the concentrations were kept low to minimize particle-particle interactions; they did, however, have to be high enough to obtain transmission differences. At 0.05 wt % concentrations, some particle-particle interactions may have occurred.

The first experiments showed that solutions of carbon black in benzene are very stable with AOT but settle reasonably well when no AOT is present (Fig. 2.6). Carbon black is a well-dispersed system in electrolyte solutions and is often used as pigment in paints and inks. By comparison, the coal-derived particles in benzene with AOT are not nearly as stable, as shown in Fig. 2.7. However, for a true comparison, the particles would have to be of similar shape, size, and density. The densities are, in fact, similar: $\rho(\text{coal-derived solids}) = 1.96$, and $\rho(\text{carbon black}) = 1.86$. The shapes are quite dissimilar. Carbon black particles approximate spheres; the axial ratio (maximum length/maximum width) of asphaltenes and (probably) asphaltene-coated particles, as indicated by previous calculations, is near 15. The particle sizes are also quite dissimilar. The effective Stokes settling diameter of Elftex carbon black is about $0.1 \mu\text{m}$; for these small diameters, Brownian motion would be significant. The particles in the wet filter cake received from the Solvent Refined Coal (SRC) plant at Wilsonville, Alabama, have a median diameter of $2.5 \mu\text{m}$ (Fig. 2.8). Stokes' law can be used to determine the relative magnitude of the settling velocities,

$$v = \frac{g d^2 (\rho_p - \rho_l)}{18\mu},$$

which are 0.084 and 59, respectively. Therefore, $\frac{v_{\text{SRC}}}{v_{\text{CB}}} = \frac{59}{0.084} \approx 700$, or, in other words, the SRC solid should settle 700 times faster than the carbon black. This explains why, for the SRC solids, the transmittance increased to ~50% in 3.3 h; the slow settling of the smaller solids accounted for the residual 50% transmittance. In three days, the transmittance increased to only 73% for the solution containing 1 millimole

Fig. 2.6. Stability of 0.05 wt % Elftex-5 carbon black in benzene.

Fig. 2.7. Stability of 0.05 wt % SRC solids in benzene.

Fig. 2.8. Particle size distribution of solids in the SRC wet filter cake.

of AOT per liter, indicating the presence of a considerable quantity of small particles.

The results for SRC particles in cyclohexane with AOT concentrations of 1 and 10 millimoles per liter are similar to those above. Settling is, however, much more dependent on the AOT concentration, as evidenced by the increased settling that occurred in the 20 mM AOT solution and in the pure solvent (Fig. 2.9). The increased settling could not be accounted for by the association of electrolyte, which would produce lower ionic mobility, because, as shown in Fig. 2.10, the conductivity increased. Apparently, the adsorption isotherm changes at higher concentration, or, perhaps, some particle coagulation occurs. The 1 mM solution had a transmittance of 78% after 24 h, whereas the 20 mM value was 96%. Thus the particles in the 1 mM solution were slightly less stable in cyclohexane than in benzene.

Figure 2.11 plots the surprising stability of the coal-derived asphaltenes in solutions of cyclohexane with AOT. These solutions were so stable that after seven days the transmittance of the AOT solutions had not changed, whereas the transmittance of the mixture of pure solvent and SRC solids had increased to 87%.

In pure solvent, the asphaltenes settled nearly three times more rapidly than did the SRC solids; the transmittance ratios (transmittance at 200 min/transmittance at 0 min) were 6.5 and 2.4, respectively, compared to about 45 for carbon black in benzene. These results clearly relate the surface charge on the particles to the settling rate. The rapid settling of carbon black in the absence of electrolyte (compared to almost complete stability in the presence of electrolyte) strongly indicates that

Fig. 2.9. Stability of 0.05 wt % SRC solids in cyclohexane.

Fig. 2.10. Conductivity vs concentration of AOT in benzene and cyclohexane solutions used in stability studies of carbon black and SRC solids.

Fig. 2.11. Stability of 0.05 wt % asphaltenes in cyclohexane.

charges exist on the surface that produce a double-layer repulsion, prevent agglomeration, and thus stabilize the particles. Of course, this is a well-known characteristic of carbon black and is the reason it is used for comparison with coal-derived solids. However, the existence and magnitude of this charge and its participation in the stabilization of SRC solids and asphaltenes had not, to the authors' knowledge, been shown prior to this work¹⁴ except through speculation¹⁵ and observations that particles are collected at the electrodes when the slurries are in an electric field.¹⁶

2.2.6 Zeta potential measurements

Considerable care was taken to obtain quantitative measurements of zeta potential for use in subsequent analyses of the effect of charge on the stability of coal-derived particles in organic media. The measurements were very sensitive, and considerable experience was required before they could be made in a reproducible manner. In retrospect, the "keys" to successful measurements were

1. using the lowest possible electric field to minimize electric heating,
2. using cool stage lighting to minimize radiant heating,
3. focusing carefully from a scratch on the bottom of the slide to determine the cell height and measuring the position of zero osmotic velocity for each sample, and
4. reversing the field after each measurement to prevent polarization, checking that the velocities were not significantly different.

Initial measurements were made on carbon black in benzene and cyclohexane that contained the organic electrolyte AOT. The purpose was to compare the results obtained using the technique developed herein with Kitahara's data, which provide one of the few data bases for particles in organic liquids. The accuracy of the current technique was proven through these measurements: the slopes of the curves of zeta potential vs AOT concentrations obtained with this technique and by Kitahara were similar, and the magnitudes of the zeta potential compared favorably. Although the agreement with Kitahara's data ranged from a maximum deviation of 30% in benzene to 50% in cyclohexane (Figs. 2.12 and 2.13), the parallel field slide and the Zeta Meter agreed to within a few percent, indicating that the variance from Kitahara's data resulted from the difference in materials rather than in apparatus and technique.

These results indicate that Kitahara missed the largest zeta potentials, which occurred at very low concentrations of AOT (1-3 mM). In cyclohexane, zeta potentials of -140 mV were obtained for the 1 mM concentration. For comparison, note that Kitahara's cyclohexane data were divided by the 1.5 factor, whereas the benzene data from this work were multiplied by this factor. This stresses the importance of indicating whether the Smoluchowski or Debye-Hückel formula is used in the calculations.

Work in quantitatively measuring coal-derived particles in coal liquids is continuing using the parallel field cell.

Fig. 2.12. Comparison of data for carbon black in benzene with AOT.

Fig. 2.13. Comparison of data for carbon black in cyclohexane with AOT.

2.3 Removal of Solids in a Granular Filter

R. E. Barker

The removal of small particles from process and waste streams is difficult and expensive. State-of-the-art technologies rely on physical properties of the solids such as size (cake filtration) and density difference (centrifuging, settling, and hydrocloning). These processes require high energy consumption for pumping the fluid through the filter cake or accelerating the solid-fluid suspension to exploit the density difference. Filtration in beds of granular solids has been used for many years for removal of small particles. In the type of filtration of interest in this study, the mechanisms mentioned above are active, but the primary mechanism of filtration involves electric interaction. Normally, the electric attraction/repulsion arises from the naturally occurring surface charge on the particles and filter media or from the addition of chemicals that change the naturally arising surface charge on the particles or media. Depending on the naturally arising charge is unreliable, and chemical additives may be expensive or may cause unacceptable contamination of the clarified stream.

A novel means of producing electric conditions favorable to particle removal is the application of an external electric field. The filter bed, made up of relatively large grains, is placed in an electric field, and the suspension is passed through the bed. As shown schematically in Fig. 2.14, the filter grains become polarized and distort the electric field in the region of the grains. Therefore, charged particles (of either sign) are attracted to the appropriate end of the uncharged polarized filter grain, and polarizable particles are polarized and

ORNL DWG 78-9898

A. HOMOGENEOUS ELECTRIC FIELD

B. FIELD DISTORTED BY POLARIZABLE OBJECT

C. ATTRACTION OF CHARGED (RIGHT) AND UNCHARGED (LEFT) PARTICLES TO A POLARIZED OBJECT

Fig. 2.14. Schematic illustrating the primary mechanism of particle removal by filtration in granular beds using an electric field.

attracted to the grain. The use of large grains allows high volumetric throughputs at very low pressure drops.

An experimental apparatus was built to study this filtration technique. The system, shown schematically in Fig. 2.15, consists of a small filter bed and the equipment necessary for applying electric fields to the bed. The feed suspension is stirred and recirculated in the feed tank; to maintain constant temperature, the feed is passed through a cooling coil in an isothermal bath. The suspension is metered through a rotameter and fed to the filter column. A small side stream of filter effluent is routed through a spectrophotometer for real-time recording of optical transmittance (an accurate measure of suspended uniform-sized solids). The filter effluent is then collected and weighed continuously (for flow-rate determination) on an electric balance. Figure 2.16 is a photograph of the system as installed. The filter column is in the upper right of the photograph; the high-voltage power supply is in the lower right; the manometer for measuring filter pressure drop is in the middle; the effluent receiver and electronic balance are seen behind the manometer; and the recorder used to record the effluent weight (integral of the flow rate) is in the foreground. Figure 2.17 is a close-up of the filter bed before the start of a run, at which point the bed and the plenums above and below the bed are filled with clear liquid, in this case, cyclohexane. By imposing a voltage on the electrodes above and below the bed, the electric field can be applied parallel to the flow. The field can also be applied perpendicular to the flow. Figure 2.18 is a photograph taken during a filtration run. Note the dark color of the suspension entering through the upper plenum and the clarity of the effluent in the lower plenum.

ORNL DWG 78-17916

Fig. 2.15. Schematic of the experimental system for studying the effect of an electric field on granular filtration.

Fig. 2.16. Photograph of the experimental system for studying the effect of an electric field on granular filtration.

Fig. 2.17. Close-up of the filter bed before start of filtration.

Fig. 2.18. Close-up of the filter bed after start of filtration.

An experimental study of filtration in granular media by an electric field is under way and has produced some interesting results. Figure 2.19 shows data obtained from filtering a 50-mg/l suspension of TiO_2 (having diameters of $\sim 1 \mu\text{m}$) in cyclohexane. Both the applied-field strength and suspension flow rate were varied. The bed material used in these experiments was 50.0 g of 1.0-mm-diam glass spheres, which produced a bed ~ 2 cm deep. By using electrodes at the tube center and at the tube wall, the electric field was applied perpendicular to the suspension flow. Note that high filtration efficiency resulted from high field strengths and low velocities. Note also that even the lower efficiencies shown for some of the less favorable conditions in Fig. 2.18 are high for a bed only 2 cm deep. When no external field was applied, the filtration efficiency was zero (or very close to zero) for all flow rates studied. The electric energy consumption of this process is extremely low; the bed draws a current of only $\sim 0.5 \mu\text{A}$.

Results to date are very promising; high filtration efficiencies are obtained with low energy consumption. This filtration method can be applied to any separation in which the suspending liquid is relatively nonconducting. Potential applications exist in the petroleum, coal conversion, and food-processing industries.

2.4 High-Temperature Slagging

S. D. Clinton

2.4.1 Introduction

Most of the important metallurgical extraction processes depend on reactions involving slag-gas-metal systems. Although the thermodynamics

Fig. 2.19. Plot of filtration efficiency (η) vs suspension approach velocity for several flow rates and field strengths.

of these reactions have, for the most part, been well established, the kinetics of these systems have not received much attention. This new study will include both development of improved slag-metal contacting equipment and the use of slagging processes in particular applications. The application of initial interest is the removal of copper from scrap metal since the presence of copper is a major problem in the recycle of many iron-base metals from several sources.

The experimental program will be directed to three areas: (1) contactor performance with mass-transfer rate limited by the extracting slag phase, (2) contactor performance with mass-transfer rate limited by the base metal phase, and (3) evaluation of slagging media for use in extracting copper from molten iron.

In the first area of research, an electrochemical technique will be used with a water-mercury system to measure aqueous-film mass-transfer coefficients augmented by gas sparging through the interface (Fig. 2.20). The variables of interest will be gas flow rate, viscosity of the aqueous phase, and contactor geometry and size. The electrochemical technique for measuring water-wide mass-transfer coefficients is based on the diffusion-limited reduction of quinone to hydroquinone at the mercury surface.

In the second area of study, a lithium-mercury amalgam-water system will be used to evaluate metal-phase mass-transfer coefficients under the same conditions. The lithium reaching the water-amalgam interface should react instantaneously to form lithium hydroxide, which should be dispersed in the aqueous phase by the rising gas bubbles. The lithium flux can then be determined by measuring the hydroxide concentration as a function of time.

Fig. 2.20. Electrochemical apparatus for simulation of slag-gas-metal contactor.

The third area of study will focus on the selection of suitable slagging media for use in extracting copper from molten iron. These initial scouting experiments will use small, simple, unagitated contactors, but subsequent experiments will combine the different aspects of this program by testing the proposed slagging materials in the agitated contactors suggested by the investigations included in the other portions of the program.

2.4.2 Program status

The electrochemical apparatus that uses a water-mercury system to simulate contactor performance with the mass-transfer rate limited by the water phase has been assembled. Initial experiments will determine the effect of the gas (nitrogen) flow rate on the aqueous-film mass-transfer coefficients in a square-cross-section contactor (10.2-cm side).

2.5 References for Section 2

1. J. S. Watson and S. D. Clinton (compilers), Advanced Technology Sect. Semiannu. Prog. Rep. Oct. 1, 1977, to Mar. 31, 1978. Volume 2: Engineering Science Programs, ORNL/TM-6377/V2 (in preparation).
2. E. J. W. Verwey and J. T. G. Overbeek, Theory of the Stability of Lyophobic Colloids, Elsevier, New York, 1948.
3. A. Kitahara, Prog. Org. Coat. 2, 81-98 (1973-74).
4. M. S. Edwards, B. R. Rodgers, and R. Salmon, Coal Technology Program, Supporting Research and Development on Separations Technology, Phase I Report, ORNL/TM-4801 (March 1975).
5. B. R. Rodgers and S. Katz, Supporting Research and Development on Separations Technology, Phase II Report: Scouting Experiments, ORNL/TM-4968 (October 1975).
6. B. R. Rodgers, S. Katz, and P. R. Westmoreland, Supporting Research and Development on Separations Technology: Final Report, ORNL/TM-5843 (October 1977).

7. A. Kitahara, T. Fujii, and S. Katano, Chem. Soc. Jpn. 44, 3242-45 (1971).
8. B. V. Derjaguin and L. Landau, Acta Physicochim. URSS 14, 633 (1941).
9. H. C. Parreira, J. Electroanal. Chem. 25, 69-78 (1970).
10. K. E. Lewis and G. D. Parfitt, Trans. Faraday Soc. 62 (521), 1652-61 (May 1966).
11. O. B. E. Garner, C. W. Nult, and M. F. Mohtodi, J. Inst. Pet. 38, 986-97 (1952).
12. H. Koelmans and J. T. G. Overbeek, Discuss. Faraday Soc. 18, 52-63 (1954).
13. M. R. Thompson, Trans. Electrochem. Soc. 81, 147 (April 1942).
14. Reported at the 84th National AIChE Meeting in Atlanta, Ga., February 1978; the 175th ACS Meeting in Anaheim, Calif., March 1978; and the ACS/CSJ Chemical Congress in Honolulu, Hawaii, April 1979.
15. R. D. Spence and J. R. Hightower, Jr., Sect. 1.6 in Experimental Engineering Sect. Semiannu. Prog. Rep., Mar. 1 to Aug. 31, 1976. Volume 3: Engineering Science Programs, ORNL/TM-5865/V3 (June 1978).
16. J. D. Henry, Jr., and M. T. Jacques, AIChE J. 23(4), 607 (1977).

3. HYDROGEN ISOTOPE TECHNOLOGY

Hydrogen and its isotopes play an important role in many advanced methods of energy and fuel production. Fusion reactors are fueled with hydrogen isotopes, and fission reactors produce radioactive tritium and use hydrogen or deuterium as moderators. Hydrogen is an important component in the liquefaction and gasification of solid and heavy-liquid fossil fuels. It has even been suggested that once carbon-based fossil fuels are depleted or when a cheap source of hydrogen is found, elemental hydrogen may become a major medium for transporting energy to its point of use.

The current program in Hydrogen Isotope Technology includes studies of vacuum pumping and tritium recovery techniques for application in fusion energy production and an analysis of hydrogen isotope separation, which is especially important in managing wastes from nuclear fission, using bipolar electrolysis with permeable electrodes. The fundamental studies of tritium sorption techniques are funded by the DOE/Office of Basic Energy Sciences. Vacuum pump development is supported by the DOE/Office of Fusion Energy, and isotope separation is funded by the DOE/Office of Waste Management.

3.1 Cryosorption Vacuum Pumping

P. W. Fisher

During this period, the program in cryosorption vacuum pumping continued work in two areas: measurement of pumping speeds for hydrogen on a molecular sieve Na-Y (MS-Na-Y) cryosorption panel at temperatures above 4.2 K and evaluation of the effects of low hydrogen concentrations on helium pumping speeds. The former tests were carried out on the variable temperature and panel apparatus described previously.¹ Tests on the

MS-Na-Y panel were completed, and the results are presented here. Helium-hydrogen runs were performed on the Excalibur cryosorption pump.² The apparatus for these experiments was modified slightly from that used previously. Results for a mixture containing 4% hydrogen--96% helium are presented.

3.1.1 Survey of sorbents and temperature for hydrogen pumping

Tests are being performed to determine the best combination of sorbent and temperature for cryosorption vacuum pumps designed to collect only hydrogen. Results for complete tests of molecular sieve 5A (MS-5A)³ and for runs at a single high feed rate for MS-Na-Y⁴ were reported previously. Tests of the MS-Na-Y panel are now complete, and a comparison of results can be made.

Maximum hydrogen pumping speed. A molecular flow model for the experimental apparatus is shown in Fig. 3.1. With this model, the pumping speed for hydrogen, S , can be calculated from

$$\frac{1}{S} = \frac{1}{F} + \frac{1}{\alpha S_0},$$

where α is the sticking coefficient, $F = 1990$ l/s, and $S_0 = 3500$ l/s. Details of the calculations are presented in ref. 1. Figure 3.2 plots pumping speed as a function of sticking coefficient. The model shows that maximum pumping speeds of about 1270 l/s should be achievable.

Experimental results. A total of 31 runs was made in two series and with different feed rates. The results are tabulated in Table 3.1 and plotted in Fig. 3.3. Before each series of runs (D and E), the system was rough pumped at room temperature to a pressure below 10^{-4} torr.

Fig. 3.1. Molecular flow model for variable panel and temperature test stand.

ORNL DWG 79-7592

Fig. 3.2. Pumping speed as a function of sticking coefficient for the variable panel and temperature test stand.

Table 3.1. Average temperature, speed, and pressure for 5-min runs on an MS-Na-Y cryosorption panel

Run	Feed rate (torr-liters/s)	Quantity of gas accumulated prior to run (torr-liters)	Average temperature at center of panel (K)	Average temperature at edge of panel (K)	Average speed (l/s)	Average pressure (torr)
D-1	6.4×10^{-3}	0	17.8	13.0	1350	5.4×10^{-6}
D-2	6.4×10^{-3}	1.9	19.8	13.7	565	1.5×10^{-5}
D-3	6.4×10^{-3}	3.8	23.9	15.8	130	6.1×10^{-5}
D-4	6.4×10^{-3}	5.8	19.6	14.0	490	1.6×10^{-5}
D-5	6.4×10^{-3}	7.7	18.0	13.0	1110	6.5×10^{-6}
D-6	1.9×10^{-1}	9.6	18.6	13.8	1140	1.9×10^{-4}
D-7	1.9×10^{-1}	66.6	19.5	14.2	690	2.8×10^{-4}
D-8	1.9×10^{-1}	123	25.4	17.9	a	a
D-9	1.9×10^{-1}	181	20.7	15.3	435	4.7×10^{-4}
D-10	1.9×10^{-1}	238	18.2	13.6	950	2.0×10^{-4}
D-11	1.1	295	20.3	16.1	1010	1.1×10^{-3}
D-12	1.1	625	20.4	16.3	1005	1.1×10^{-3}
D-13	1.1	955	26.5	18.2	a	a
E-1	4.5×10^{-3}	0	18.5	12.7	1435	3.3×10^{-6}
E-2	4.5×10^{-3}	1.3	18.5	14.0	990	5.3×10^{-6}
E-3	4.5×10^{-3}	2.7	20.2	18.2	220	2.6×10^{-5}
E-4	4.5×10^{-3}	4.0	24.7	23.2	35	1.4×10^{-4}
E-5	4.5×10^{-3}	5.4	18.1	12.8	1195	4.1×10^{-6}
E-6	4.3×10^{-2}	6.7	18.2	12.7	1360	3.2×10^{-5}
E-7	4.3×10^{-2}	19.6	19.1	14.4	345	1.3×10^{-4}
E-8	4.3×10^{-2}	32.5	22.0	18.7	90	5.8×10^{-4}
E-9	4.3×10^{-2}	45.4	25.3	23.4	40	1.2×10^{-3}
E-10	4.3×10^{-2}	58.3	18.0	12.8	1365	3.2×10^{-5}
E-11	3.9×10^{-1}	71.2	19.3	13.6	1105	3.5×10^{-4}
E-12	3.9×10^{-1}	188	19.4	14.0	1070	3.6×10^{-4}

Table 3.1 (Continued)

Run	Feed rate (torr-liters/s)	Quantity of gas accumulated prior to run (torr-liters)	Average temperature at center of panel (K)	Average temperature at edge of panel (K)	Average speed (l/s)	Average pressure (torr)
E-13	3.9×10^{-1}	305	23.7	20.5	<i>a</i>	<i>a</i>
E-14	3.9×10^{-1}	422	22.4	17.8	430	9.5×10^{-4}
E-15	3.9×10^{-1}	539	24.5	26.2	<i>a</i>	<i>a</i>
E-16	3.9×10^{-1}	656	23.7	21.3	<i>a</i>	<i>a</i>
E-17	3.9×10^{-1}	773	19.5	13.8	<i>a</i>	<i>a</i>
E-18	3.9×10^{-1}	890	18.1	12.8	975	5.4×10^{-6}

^aUnstable variations in speed and pressure occurred.

Fig. 3.3. Average pumping speeds vs average temperatures for 5-min runs for the MS-Na-Y and MS-5A panels. Data plotted for the MS-5A panel represent the range of experimental data at the indicated temperature.

Each run was preceded by low-temperature surface activation, which involved heating the panel to 40 K and recooling to allow material collected on the surface to migrate into the bulk of the sorbent.

Discussion. As shown in Fig. 3.3, the centerline and edge temperatures of the MS-Na-Y panel differed significantly. The cause of this temperature gradient is not known, and every attempt made to alleviate it failed. Table 3.2 compares germanium resistance thermometer (GRT) and thermocouple readings taken during several runs in which different panels, chevrons, and heat-sinking methods were used. There was not a thermocouple at the edge of the MS-5A panel. The GRT readings at the center and edge of the panel agreed well with each other; however, the GRT readings were much higher (12 to 20 K higher) than the thermocouple readings. In the MS-5A panel, the GRTs were not in good thermal contact with the panel; only about half their length penetrated into the surface. In the MS-Na-Y panel, the GRTs always read about 5 K hotter than the thermocouples. Also, the entire length of the GRTs penetrated into the panel, which gave better, but not perfect, thermal contact. The approximately 5 K temperature differential between the outside edge and the centerline temperatures was recorded by both the GRTs and the thermocouples. Results for runs B and C are about the same even though all the instrumentation was removed and remounted on the panel between these series of runs and the chevron temperature was lowered by almost 100 K. It was thought that changing the direction of the flow of the liquid helium coolant on the back of the panel would eliminate the problem of the center being hotter than the edge. For the runs reported here, the flow was switched from the radially inward pattern used on all runs reported

Table 3.2. Comparison of thermocouple and GRT readings

Run	Chevron	Temperature (K)			
		At centerline		At edge	
		Thermocouple	GRT	Thermocouple	GRT
Prior to MS-5A run B-1	130	11.7	24		25.5
MS-5A run D-3	130	12.5	25		26
MS-5A run D-8	130	20.2	28		29
Prior to MS-Na-Y run B-1	175	17.3	24	12.8	18
MS-Na-Y run B-1	175	18.1	24	13.2	18.8
MS-Na-Y run B-3	175	30	30	32.1	30
MS-Na-Y run B-5	175	19.1	24	14.2	19
MS-Na-Y run C-1	79	16.3	18	10	14.5
MS-Na-Y run C-4	79	16.4	17.5	9.9	14.5

previously to radially outward. The instrumentation was also removed and remounted while these changes were made. Table 3.1 and Fig. 3.3 show that the temperature gradient persisted even after these changes. It must be concluded, therefore, that the temperature gradient is real.

Apparently, the surface temperature in these panels is not homogeneous, and an exact definition of "a single surface temperature" is impossible. The low thermal conductivity of the stainless steel and molecular sieve combined with poor bonding between the two materials could lead to such temperature variations. Temperature variations caused by these effects need not be symmetrical; the temperature at one point near the outside edge is not necessarily the temperature of the entire perimeter.

Obviously, better control of the surface temperature is desirable; however, it may not be achievable here or in practice. Improved substrates and bonding techniques could provide thermal homogeneity in the future, but other problems exist in the current apparatus. Figure 3.4 compares liquid helium utilization in the Excalibur pump, which operates at 4.2 K, with that in the variable temperature pump operating at temperatures above 10 K (we were not able to reach lower temperatures). Cooling power for the Excalibur pump is defined here as the heat required to vaporize the liquid plus the heat required to raise the temperature of the gas to 20 K in the chevron. Cooling power for the variable temperature pump is the heat required to vaporize the liquid helium and raise the temperature of the gas to the operating temperature of the panel minus the heater power delivered to the back of the panel. The variable temperature pump requires about two orders of magnitude more liquid helium than the

Fig. 3.4. Cooling power delivered to the cryosorption panel in the variable panel and temperature apparatus as a function of operating pressure. The dashed line plots similar data measured previously for the Excalibur pump.

Excalibur pump. Apparently, a thermal "short" exists in the helium delivery system that prevents the panel from reaching the lowest desired temperatures. This "short" may also affect the temperature uniformity of the panel.

Conclusions. The comparison of pumping speeds for MS-5A and MS-Na-Y made in Fig. 3.3 reveals that, at worst, these two materials will perform similarly and that, at some conditions at low temperatures, the MS-Na-Y could offer an order of magnitude improvement in performance over MS-5A.

Program status. An MS-13X panel was installed in the apparatus for testing in the near future.

3.1.2 Compound pump development for hydrogen-helium mixtures

Previous studies^{1,2} showed that mixtures of hydrogen and helium at the compositions expected in fusion reactors (1 to 15% helium) cannot be accommodated by an MS-5A cryosorption panel at 4.2 K if the helium feed rate is above the critical feed rate for helium instabilities,⁵ or, in other words, if $Q_{\text{He}} > 6 \times 10^{-6}$ torr-liter/s·cm². Hydrogen accumulating at the surface of the cryosorption panel prevents helium from being adsorbed. These findings led to the development and testing^{1,2} of the compound pump concept. In this concept, hydrogen is removed from the gas mixture by a cryosorption or cryocondensation pump located in front of the helium cryosorption pump. Design of the hydrogen pump in such an array must be optimized to give maximum concentration to the helium panel while adequately protecting the panel from hydrogen. The purpose of the current study is to determine how much hydrogen can be admitted to the cryosorption panel.

Experimental apparatus. The experimental apparatus used in these studies is shown in Fig. 3.5. The Excalibur CVR 1106 cryosorption pump, test chamber, and roughing system were described in previous reports.^{6,7} In this apparatus, feed gas is supplied through a pair of calibrated orifices, and the feed rate is controlled by the pressure at the inlet of the orifice. Calibrations obtained for helium and hydrogen from 0 to 100 psig showed little difference. A gas analysis system, consisting of a UTI quadrupole mass spectrometer (MS), ion pump, and roughing pump, is attached to both the feed gas system and the test chamber. To avoid excessive helium accumulation in the gas analysis system, gas is withdrawn from the apparatus only for the time required to make an MS scan. The MS was calibrated by using known mixtures in the feed gas system.

Experimental results and discussion. Table 3.3 summarizes the seven runs made in this program to date. Two runs (A-1 and A-2) with helium at feed rates just above and just below the critical feed rate for helium instabilities were made for comparison with previous helium data.⁵ In Fig. 3.6, the results for the seven runs are plotted with the previous data. The accumulations per cycle in these new data are a factor of about 1.5 higher than those in the old data; extrapolation from data at higher feed rates may show that this is within experimental error. Accumulations per cycle for the 4% hydrogen--96% helium mixture lie above all previous helium data. A small amount of hydrogen in the helium, then, does not hinder, but may actually increase, the amount of helium collected prior to (and between) instabilities. Pumping speeds have not yet been calculated from these data.

Fig. 3.5. Experimental apparatus for measuring mixed gas pumping speeds.

Table 3.3. Mixed gas pumping results

Run	Feed gas	Total feed rate, Q (torr-liters/s)	Helium feed rate, Q_{He} (torr-liters/s)	Run time, no instability (h)	Run time between instabilities (h)			
					Instability number			
					1	2	3	4
A-1	Helium	2.11×10^{-3}	2.11×10^{-3}	27.8				
A-2	Helium	3.72×10^{-3}	3.72×10^{-3}		17.1	16.0		
B-1	4.2% H ₂ --95.8% He	2.13×10^{-3}	2.04×10^{-3}	27.8				
B-2	4.2% H ₂ --95.8% He	3.72×10^{-3}	3.56×10^{-3}		24.4			
B-3	4.2% H ₂ --95.8% He	3.76×10^{-3}	3.59×10^{-3}		20.7			
B-4	4.2% H ₂ --95.8% He	1.23×10^{-2}	1.18×10^{-2}		2.9			
B-5	4.2% H ₂ --95.8% He	2.55×10^{-2}	2.44×10^{-2}		1.6	1.0	0.92	0.92

Fig. 3.6. Helium accumulation per cycle as a function of helium feed rate.

There is a much larger spread in data in run B-5 than was observed in the data for pure helium. Figure 3.7 shows cycle length vs cycle number for this run and for a pure helium run at the same feed rate. Behavior of the pump is quite different for the two conditions. Why the mixture curve should lie above the pure gas curve is not known; however, the trends observed in each curve can be explained.

The curve for pure helium shows increasing length with time. An explanation of this behavior is that the adsorption capacity of the cryosorption panel is increasing because the temperature of the face of the cryosorption panel is decreasing. Such an effect could be a result of reduced heat transfer from the cryosorption panel to the inner chevron. The inner chevron is cooled by boil-off from the liquid helium reservoir; during normal operation, its temperature is about 20 K. However, the boil-off rate increases substantially during runaways, causing the inner chevron to approach 4.2 K. Each successive runaway causes the inner chevron to get cooler, which, in turn, causes the next pumping cycle to be longer.

The mixture data in Fig. 3.7 show a monotonic decrease in cycle length with time. The first cycle for the hydrogen-helium mixture is substantially longer than the first cycle for pure helium. The reason the mixture shows this improvement with time is not known; however, this enhancement should continue from cycle to cycle. A possible reason for reduction in cycle length is that cryogenic runaway, which occurs between cycles, separates the gas constituents. When an instability occurs, both hydrogen and helium are released from the panel. During the cryogenic runaway, the inner chevron is cooled (by boil-off gas from the liquid helium reservoir), and the cold chevron collects the hydrogen released from the panel. When

Fig. 3.7. Helium accumulation per cycle as a function of cycle number for pure helium and a mixture containing 4% hydrogen for run B-5.

the panel recools, it first collects the helium gas it released; then, when the pressure in the system declines and liquid helium boil-off ceases to cool the inner chevron, the hydrogen is released from the chevron and deposited on the front of the cryosorption panel. Hydrogen, therefore, has a more significant blocking effect on helium accumulation after the first "runaway" because it is segregated from the helium and covers the surface of the cryosorption panel.

Figure 3.8 shows the hydrogen concentration in the system (measured on the upstream side of the orifice plate) as a function of time until the next runaway (time is proportional to accumulation at constant feed rate). The first run starts at the far right; successive runs start near the middle of the abscissa and progress toward the left. Instabilities occur when zero helium capacity is reached. At the time of instability, the hydrogen concentration is about 0.85 vol %; hydrogen concentrations are always much lower than the feed. Figure 3.9 shows another representation of the same data. Here the hydrogen concentration is plotted as a function of elapsed time; the line is drawn to match the line in Fig. 3.7. Apparently, after the first runaway pump behavior is periodic.

Pumping speeds have not yet been calculated from these data; however, the low hydrogen concentrations observed in the test chamber can be explained by previously measured speeds for pure hydrogen and helium. The pumping speed for hydrogen at this feed rate is relatively constant at about 1250 ℓ/s , whereas the speed for helium varies periodically from about 550 ℓ/s to 200 ℓ/s just before an instability. The hydrogen speed is essentially conductance limited, but the helium speed is far below its conductance-limited value of about 1000 ℓ/s . The consequence of this

Fig. 3.8. Hydrogen concentration in the test chamber as a function of helium capacity (time) until the next cryogenic runaway for run B-5.

Fig. 3.9. Hydrogen concentration in the test chamber as a function of time during run B-5.

behavior is that, for a given feed rate, hydrogen would have a lower pump inlet pressure than helium. The same holds true for a gas mixture. The hydrogen-to-helium ratio in the feed will always be higher than the concentration in the system as long as the pumping speed for hydrogen is higher than that for helium. Judging from pumping speed data for pure components, one would expect the feed composition of 4.2 vol % hydrogen to produce concentrations in the test chamber of 2.1 to 2.7% hydrogen. Because even lower hydrogen compositions (0.9 to 1.6 vol %) were observed (Fig. 3.8), the pumping speed for helium in the mixture seems to be lower than that observed for pure helium. Therefore, although the presence of hydrogen at the 4.2% level increases the length of time between instabilities, it adversely affects the helium pumping speed during this time.

Status of work. Tests are continuing to determine the maximum concentration of hydrogen in helium that can be admitted to the helium cryosorption pump. Data are also being analyzed to determine pumping speeds.

3.2 Tritium Recovery from Yttrium Getters

J. B. Talbot

One of the most promising techniques for recovering tritium from a fusion reactor blanket of liquid lithium involves sorption on a hydrogen-gettering metal, such as yttrium. Tritium sorption from liquid metal was studied in a batch contactor at 250 to 400°C using metal sorbent samples of yttrium.⁸ The results indicated that a moderately high rate of tritium removal occurred, which demonstrated the feasibility of such a blanket-recovery process system. However, if yttrium is used for the sorption of tritium from liquid lithium, the tritium must ultimately be recovered from the getter material.

3.2.1 Experimental apparatus

The method being studied for recovering tritium from yttrium getters involves heating the yttrium in the presence of an inert sweep gas to temperatures well above the sorption temperature. Initially, the yttrium samples were contacted with tritiated liquid lithium. The release rate is being investigated at different temperatures in a system used previously to study tritium removal from irradiated lithium-containing aluminum and sintered aluminum product.⁹ A tritiated sample of yttrium is heated to the desired temperature while preheated argon flushes the released tritium to a tritium monitor. The released tritium is then fed through a trapping system composed of a copper oxide bed (at 600°C) and two water bubblers in series. Another tritium monitor detects any tritium release from the trapping system, which ultimately leads to the radioactive off-gas stack.

3.2.2 Results and discussion

The tritium release rate was measured for one sample of yttrium at 505°C. The concentration of tritium in the sample (~ 0.56 g, 2.22 cm²) was 9.0 ppm. The percentage of tritium released is shown in Fig. 3.10. Although only 0.153% of the tritium was released after 21 h, this was a "low temperature" run, only 100°C above the sorption temperature, and rapid release was not expected. The temperature in this initial run was limited by the capabilities of the system's existing furnace. Higher temperatures, which will increase both the driving pressure and the permeability of the samples, will be needed to increase the recovery rate.

3.2.3 Program status

The experimental apparatus was modified to include a furnace capable of reaching much higher temperatures. The tritium monitor was sent to

Fig. 3.10. Tritium release from yttrium at 505°C.

the manufacturer for repair and recalibration during August 1978 and should be returned and installed during November 1978. In future runs, samples will be heated to temperatures ranging to 800°C.

3.3 Tritium Sorption from Liquid Metals

J. B. Talbot

A molten-lithium blanket is one of the best means of breeding tritium in fusion reactors. One of the techniques being considered for recovering tritium from liquid lithium involves sorption on a hydrogen-gettering metal. Tritium sorption from molten lithium was studied in a batch contactor at temperatures of 250 to 400°C using samples of yttrium metal.⁸ With the static system, significant removal rates were achieved. Because the controlling mass-transfer resistance appears to be in the liquid lithium phase, the mass-transfer rate could be increased significantly by forced convection. A new contacting system was assembled in the existing glove box and loaded with 1200 g of lithium.

3.3.1 Experimental apparatus

Figure 3.11 is a schematic diagram of the equipment used to contact flowing tritiated liquid lithium with yttrium metal. The equipment consists of a tritiated liquid-metal reservoir, a liquid-metal sampling tank, a contacting chamber, an electromagnetic pump and flowmeter, a vacuum source, and an argon supply. Tritiated lithium is drawn from a liquid-metal reservoir into a transfer tank at temperatures between 200 and 400°C. The liquid lithium is then electromagnetically recirculated through a flowmeter and a sample chamber holding the yttrium sample. The liquid lithium is sampled by placing a tube attached to a rod into the transfer lock formed

Fig. 3.11. Contacting apparatus for tritium sorption studies using forced convection of lithium.

by an O-ring seal and ball valve. The lithium samples are dissolved in water, the evolved tritium is oxidized, and the resulting solutions are analyzed for tritium by scintillation counting. The entire lithium loop is enclosed in an inert-atmosphere glove box; the box reduces oxygen and nitrogen contamination and serves as secondary tritium containment.

3.3.2 Program status

A 1200-g batch of purified lithium was obtained from the ORNL Metals and Ceramics Division. The heaters for the lithium system were installed and checked. On completion of insulation and a check of glove box operation, the lithium will be recirculated and sampled to test the operating procedure. Then tritium will be added to the lithium, and the sorption tests in yttrium will begin during November 1978.

3.4 Hydrogen Isotope Separation in Aqueous Systems Using Bipolar Electrolysis with Hydrogen-Permeable Electrodes

P. W. Fisher

The separation of hydrogen isotopes from aqueous systems is an important technology for both heavy-water production and tritium recovery from fission and fusion reactor coolant streams. Many processes have been proposed and used to accomplish these separations.¹⁰ Several chemical, physical, and even biological systems exhibit isotopes effect, which is when one of the hydrogen isotopes contained in water is either reacted, transferred, or assimilated more rapidly than another. Examples of these systems include electrolysis, exchange reactions, and distillation. Most of the processes used contain several complimentary steps (e.g., dissociation of water followed by exchange reaction) each of which exhibits an

isotope effect in the same direction. In addition, most are multistage operations. Bipolar electrolysis with hydrogen-permeable electrodes (BEPE) should combine the best attributes of electrolysis, gas permeation, and multistage operation into a single cell. Electrolysis and permeation both favor enrichment of the lighter isotope. This work will analyze the BEPE process and will provide an analytical model for determining separation factors from experimental data.

3.4.1 Background

Bipolar electrolysis is commonly used to produce hydrogen and oxygen from water. Figure 3.12 shows a schematic diagram of a bipolar cell. The bipolar electrode has both a cathodic and anodic side induced by the current flow between the terminal electrodes. The terminal electrodes in the bipolar cell function the same as the electrodes in cells that produce hydrogen on the cathodic side and oxygen on the anodic side. However, in the bipolar cells, a gas barrier between adjacent electrodes prevents the hydrogen and oxygen from recombining. These cells are attractive because the surface area available for gas production can easily be increased by interposing additional bipolar electrodes between the terminal electrodes. Hydrogen and oxygen are produced at the same rate between each pair of electrodes because the current is the same through each electrode. Inlet (H_2O) and outlet (H_2 and O_2) streams are connected in parallel throughout the cell.

The BEPE process for isotope separation examined in this report, which is also illustrated in Fig. 3.12, differs from ordinary bipolar electrolysis in that the bipolar electrode is made of a metal that is highly permeable to hydrogen. The current density in these cells is

Fig. 3.12. Comparison between a bipolar water electrolysis cell and a bipolar water electrolysis cell with a hydrogen-permeable electrode. Reactions are shown for basic electrolyte.

kept below the rate of hydrogen permeation through the bipolar electrode. The hydrogen permeating through the electrode combines with oxygen on the other side, and neither hydrogen nor oxygen gas is produced at the bipolar electrode. Therefore, hydrogen produced on the cathodic side of the bipolar electrode permeates through the electrode and recombines with hydroxyl ions on the anodic side as they lose their electrons. Gas is evolved only at the terminal electrodes. This concept is easily extendable to multistage operation because water can be circulated countercurrent to the hydrogen flow between the bipolar electrodes. The BEPE concept was demonstrated by Salmon¹¹ for D₂O/H₂O separation in a single-stage cell using a bipolar palladium electrode. The concept was extended to multistage cells by Ramey, Petek, and Kobisk.¹² Feasibility for D₂O/H₂O and T₂O/H₂O separations using 75% palladium--25% silver bipolar electrodes was demonstrated experimentally;¹² some of these results are analyzed here.

3.4.2 Estimations of the maximum current densities from permeation rates of hydrogen and deuterium through 75% palladium--25% silver

The following reactions occur at an ordinary (impermeable) bipolar electrode in basic solution:

When hydrogen-permeable bipolar electrodes are used, these reactions can also occur:

overall: no reaction .

Equations (1) and (3) are competing reactions on the cathodic side of the bipolar electrode. If the permeation of hydrogen atoms through the electrode [Eqs. (3) and (4)] maintains sufficient hydrogen activity on the anodic side of the bipolar electrode, then the rate of recombination [Eq. (1)] will be sufficient to prevent O_2 formation. If the permeation rate is not adequate, then ordinary electrolysis will occur. The maximum current density in a BEPE cell is, therefore, limited by the hydrogen permeability of the bipolar electrode.

Ramey¹³ determined the permeation rate of both hydrogen and deuterium through 75% palladium--25% silver alloy at temperatures between 200 and 325°C and pressures between 200 and 8000 psia:

$$R(\text{H}_2) = 1944(\Delta\sqrt{P})^{1.085} \frac{A}{t} \exp[-1866(\Delta\sqrt{P})^{0.0887}/T] , \quad (5)$$

$$R(\text{D}_2) = 35.23(\Delta\sqrt{P})^{1.931} \frac{A}{t} \exp[-685(\Delta\sqrt{P})^{0.326}/T] . \quad (6)$$

If extrapolated to conditions suitable for the BEPE process, Eqs. (5) and (6) give permeation rates of

$$\frac{R(\text{H}_2)}{A} = 57.2 \frac{\text{cc(STP)}}{\text{in.}^2 \cdot \text{min}} ,$$

$$\frac{R(\text{D}_2)}{A} = 7.3 \frac{\text{cc(STP)}}{\text{in.}^2 \cdot \text{min}} ,$$

assuming a hydrogen pressure of 14.7 psia on the cathodic side of the membrane and zero on the anodic side, $t = 1.97$ mills, and a temperature of 300 K. These permeation rates can be converted to current densities through the use of Faraday's equation to yield

$$\frac{I(\text{H}_2)}{A} = 0.08 \text{ A/cm}^2 ,$$

$$\frac{I(\text{D}_2)}{A} = 0.16 \text{ A/cm}^2 .$$

As can be seen, the estimated maximum allowable current densities at 27°C (300 K) are much lower than the proposed 0.5 A/cm² operational level. Also note that the permeation rate for D₂ is higher than that for H₂, indicating that permeation will work against electrolysis at this temperature. Further examination of the behavior of Eqs. (5) and (6) indicates that H₂ and D₂ have the same permeation rate at 94°C; furthermore, this rate corresponds to 0.3 A/cm², which is an acceptable current density. Therefore, operation at temperatures above 94°C is desirable.

3.4.3 Analysis of experimental data

Figure 3.13(a) diagrams a multistage BEPE cell containing four hydrogen-permeable bipolar electrodes and a terminal anode and cathode. Stream F is the feed to the cell. Water is circulated from compartment to compartment, countercurrent to the hydrogen (and current) flow through the bipolar electrodes. P is the product stream, which is enriched in the heavy-hydrogen isotope. Stream W recombines the hydrogen and oxygen gas from the terminal electrodes into a liquid stream enriched in light isotope. Figure 3.14 plots typical experimental data for the BEPE separation of D₂O from H₂O in this cell; details of the experiment are given elsewhere.¹⁴ Important parameters for the experiment are shown in the figure. Also note that mole fractions are for H₂O; the electrolyte was NaOH; and flow rates were not corrected for the presence of NaOH. Table 3.4 tabulates the data for the nine days of steady-state operation;

ORNL-DWG 79-7581

Fig. 3.13. BEPE cell with four hydrogen-permeable bipolar electrodes: (a) schematic of experimental cell showing control volumes for idealized stages and (b) idealized representation of cell drawn vertically to show analogy to stripping section of a distillation column.

Fig. 3.14. Experimental results for a four-membrane BEPE separation of D_2O/H_2O .

Table 3.4. Experimental data for four-membrane BEPE separation of D₂O/H₂O during nine days of steady-state operation

Stream	Units	Estimated standard deviation (%)	Day								
			1	2	3	4	5	6	7	8	9
F	Moles H ₂ O per day	<u>+8</u>	1.26	1.26	1.26	1.26	1.26	1.26	1.26	1.26	1.26
W	Moles H ₂ O per day	<u>+12</u>	0.61	0.61	0.61	0.61	0.61	0.61	0.61	0.61	0.61
P	Moles H ₂ O per day	<u>+8</u>	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65
X _F	Mole fraction H ₂ O	<u>+4</u>	0.800	0.800	0.800	0.800	0.800	0.800	0.800	0.800	0.800
X _W	Mole fraction H ₂ O	<u>+4</u>	0.975	0.978	0.971	0.970	0.972	0.968	0.970	0.971	0.972
X _P	Mole fraction H ₂ O	<u>+4</u>	0.700	0.710	0.68	0.70	0.690	0.700	0.715	0.705	0.710

error estimates were provided by Ramey.¹⁵ Flow rates in this table were corrected to include the hydrogen in the electrolyte. To determine the best values of the various flow rates and composition, data from Table 3.4 were analyzed using the method of Barker.¹⁶ The adjusted steady-state data are presented in Table 3.5. Average values for the nine days of operation (last column) were used in the following evaluation.

The model. For this analysis, it is assumed that the separation factor α for the hydrogen-permeable bipolar electrode may differ from that of the terminal electrolysis cell [stage 1, Fig. 3.12(a)], which is designated α_E . The separation factor is defined by

$$\alpha = \frac{y/(1 - y)}{x/(1 - x)} , \quad (7)$$

where x is the mole fraction of the light component in the liquid phase and y is its mole fraction in the electrolytically produced gas that either permeates through the membrane in the bipolar stages or is evolved in the terminal stage. When cast in this manner, the BEPE cell becomes analogous to the stripping section of a distillation column with relative volatility α and α_E in corresponding stages. This analogy is depicted in Fig. 3.13(b). The purpose of the following analysis is to determine the separation factors from the flow rates and compositions of inlet and outlet streams; the analysis, however, will be kept general so that α for each individual stage can be determined from interstage compositions.

Referring to Fig. 3.13(b), the light-component mass balances for the indicated control volumes are

$$Gy_5 = Lx_4 - Px_5 ,$$

Table 3.5. Adjusted data from Table 3.4

Stream	Units	Day									Average
		1	2	3	4	5	6	7	8	9	
F	Moles H ₂ O per day	1.260	1.260	1.260	1.260	1.260	1.260	1.260	1.260	1.260	1.260
W	Moles H ₂ O per day	0.603	0.602	0.605	0.604	0.604	0.604	0.602	0.603	0.602	0.603
P	Moles H ₂ O per day	0.657	0.658	0.655	0.656	0.656	0.656	0.658	0.657	0.657	0.657
X _F	Mole fraction H ₂ O	0.820	0.824	0.813	0.819	0.816	0.813	0.823	0.821	0.823	0.820
Y _E	Mole fraction H ₂ O	0.960	0.961	0.962	0.956	0.960	0.955	0.953	0.956	0.956	0.958
X _P	Mole fraction H ₂ O	0.592	0.700	0.675	0.692	0.683	0.693	0.705	0.697	0.701	0.693

$$Gy_4 = Lx_3 - Px_5, \text{ etc.} \quad (8)$$

Rearranging Eq. (8), we obtain

$$y_5 = \frac{L}{G}x_4 - \frac{P}{G}x_5, \\ y_4 = \frac{L}{G}x_3 - \frac{P}{G}x_5, \text{ etc.} \quad (9)$$

The set of mass balance equations is identical to those developed for the McCabe-Thiele method for multistage distillation. Constant molal overflow occurs because the upward flux of material in the bipolar cell is equal to the current flow I and is the same for all stages:

$$I = nFW = nFG, \quad (10)$$

where n is the number of equivalents per mole and F is Faraday's constant.

From Eq. (10), we see that

$$G = W. \quad (11)$$

The overall mass balances are

$$F = W + P, \\ L = G + P = W + P = F. \quad (12)$$

If we substitute Eqs. (11) and (12) into Eq. (9),

$$y_5 = \frac{F}{W}x_4 - \frac{P}{W}x_5, \\ y_4 = \frac{F}{W}x_3 - \frac{P}{W}x_5, \text{ etc.} \quad (13)$$

Unique values for α_E and α are not known and cannot be determined directly from the data because only the overall flow rates and compositions of the streams are known. We will consider two cases. In the first, it is assumed that α_E equals α , or, in other words, that the end electrodes act just like the bipolar electrodes. The second case assumes that all bipolar electrodes have the same α but that the terminal electrodes have a separation factor α_E . A program was written that uses the available data for a run to solve for α_E for a given value of α by using Eqs. (7) and (13); results of this program are shown in Fig. 3.15. Figures 3.16 and 3.17 show the McCabe-Thiele diagrams for two assumed values of α_E . Note that the slope of the operating line [F/W in Eq. (13)] is very large, creating a pinch at the equilibrium line. Both curves indicate that most of the separation takes place in two stages. Figure 3.18 shows the predicted liquid-phase compositions for each stage in the cell. If liquid-phase compositions had been measured, there would be no problem distinguishing between these two models. In fact, if liquid-phase compositions are measured, no assumption need be made about α because it can then be determined for each stage directly from the data.

In T_2O/D_2O and T_2O/H_2O separations, tritium may have to be recovered from streams with very low concentration. The data for such separations can be analyzed using the model described above; however, graphical representation of the results in log-log form would be more accurate. Figure 3.19 shows the McCabe-Thiele diagram for a T_2O/H_2O separation carried out in a cell similar to that shown in Fig. 3.13(a); details of this experiment are given elsewhere.¹⁷ As determined from the computer model and the experimental inlet and outlet, the value of α was 6.53

Fig. 3.15. Combinations of α and α_E that satisfy the McCabe-Thiele analysis determined from the average of the adjusted experimental data shown in Table 3.5.

ORNL-DWG 79-7588

Fig. 3.16. McCabe-Thiele diagram for the four-membrane (five-stage) BEPE experimental cell assuming $\alpha = \alpha_E = 5$.

ORNL-DWG 79-7586

Fig. 3.17. McCabe-Thiele diagram for four-membrane (five-stage) BEPE experimental cell assuming $\alpha \neq \alpha_E = 7$.

ORNL-DWG 79-7587

Fig. 3.18. Liquid stream compositions predicted from the assumptions for α_E shown in Figs. 3.16 and 3.17.

Fig. 3.19. McCabe-Thiele diagram for T_2O/H_2O separation in a four-membrane (five-stage) BEPE cell assuming $\alpha = \alpha_E$.

when α_E was assumed to equal α . Because x and y are about unity, the tritium concentrations ($1-x$ and $1-y$) are plotted rather than the protium concentrations. This places the equilibrium curve below the 45° line. Note that the operating line, from Eq. (13), is curved in this type of plot, and the equilibrium line, from Eq. (7), is straight. After steady-state operation was achieved, the experiment was terminated and the compartments were drained and analyzed. The results are plotted in Fig. 3.20 along with the predicted liquid-phase compositions from Fig. 3.19. Agreement is very good!

Total reflux experiments in BEPE cells. More accurate information about separation factors could be obtained from the experimental data if the slope of the operating line were closer to or equal to one. This, however, cannot be accomplished in a cell that operates as a stripping section because electrolyte accumulates in the last stage. We therefore recommend that an experiment be operated as an enriching section so electrolyte accumulation will not be a problem. Once values of α are determined from the enriching experiments, they can be used to design both enriching and stripping sections.

Figure 3.21 shows schematic flow diagrams for a bipolar electrolysis cell operated as an enriching section under total reflux. As shown in Fig. 3.21(a), the hydrogen produced at the cathode is oxidized and returned to the first cell. Electrolyte can be introduced into this cell as Na_2O or sodium metal, which will not alter the hydrogen isotope composition of the water. Electrolyte composition in the anode compartment can be controlled by the F and P streams.

From the mass balances for the control volumes shown in Fig. 3.21(b), we see that

Fig. 3.20. Comparison between McCabe-Thiele predictions (-) for liquid stream compositions and actual analysis (•) of water drained from compartments after completion of experiment.

ORNL-DWG 79-7582

Fig. 3.21. Proposed total reflux BEPE experiment: (a) schematic of experimental cell and (b) idealized analogy to enriching section of a distillation column.

$$x_i = y_{i+1} ,$$

$$L = G = W ,$$

$$x_F = x_5 . \quad (14)$$

Figures 3.22 and 3.23 present McCabe-Thiele plots for two hypothetical systems for which the α and α_E values were assumed to be the same as those used in Figs. 3.15 and 3.16. The feed composition was assumed to be $x_F = 0.02$. Operation in this mode yields information about the entire equilibrium curve. Figure 3.24 shows the stream compositions for these hypothetical systems; if interstage compositions were determined, one could then simply and accurately distinguish between models. A comparison of Figs. 3.24 and 3.18 demonstrates how much more powerful data from the enriching section can be in evaluating the bipolar electrode process than those from the stripping section.

3.4.4 Conclusions

Accurate separation factors can be determined from BEPE experiments using the McCabe-Thiele method. Two experiments were analyzed, and it was found that $\alpha = \alpha_E = 5$ provides an adequate representation of the data for D_2O in H_2O at 250 mA/cm^2 and that $\alpha = \alpha_E = 6.53$ gives an adequate representation for T_2O in H_2O at 300 mA/cm^2 . Interstage concentrations for the latter experiment confirm that $\alpha = \alpha_E$ is a good assumption.

Maximum current densities were estimated to be 0.3 A/cm^2 for both H_2O and D_2O at 94°C .

ORNL-DWG 79-7584

Fig. 3.22. McCabe-Thiele diagram for a total reflux experiment in which $x_F = 0.02$ and $\alpha = \alpha_E = 5$.

ORNL-DWG 79-7585

Fig. 3.23. McCabe-Thiele diagram for a total reflux experiment in which $x_F = 0.02$, $\alpha_E = 7$, and $\alpha = 1.67$.

ORNL-DWG 79-7583

Fig. 3.24. Liquid stream compositions predicted from the two values assumed for α_E in the proposed total reflux experiments shown in Figs. 3.21, 3.22, and 3.23.

3.5 References for Section 3

1. J. S. Watson and S. D. Clinton (compilers), Advanced Technology Sect. Semiannu. Prog. Rep. Sept. 1, 1976, to Mar. 31, 1977. Volume 2: Engineering Science Programs, ORNL/TM-6012/V2 (December 1978).
2. P. W. Fisher and J. S. Watson, "Cryosorption Pumping of 95% Deuterium--5% Helium on Molecular Sieve-5A at 4.2 K," Proceedings of the Seventh Symposium on Engineering Problems of Fusion Research, CONF-771029-84, p. 1816 (October 1977).
3. J. S. Watson and S. D. Clinton (compilers), Advanced Technology Sect. Semiannu. Prog. Rep. Apr. 1, 1977, to Sept. 30, 1977. Volume 2: Engineering Science Programs, ORNL/TM-6328/V2 (November 1979).
4. J. S. Watson and S. D. Clinton (compilers), Advanced Technology Sect. Semiannu. Prog. Rep. Oct. 1, 1977, to Mar. 31, 1978. Volume 2: Engineering Science Programs, ORNL/TM-6377/V2 (in preparation).
5. P. W. Fisher and J. S. Watson, "Helium Pumping at 4.2 K by Molecular Sieve 5A," J. Vac. Sci. Technol. (January/February 1979).
6. C. D. Scott et al., Experimental Engineering Sect. Semiannu. Prog. Rep. (Excluding Reactor Programs), Mar. 1, 1975, to Aug. 31, 1975, ORNL/TM-5291 (September 1976).
7. C. D. Scott et al., Experimental Engineering Sect. Semiannu. Prog. Rep. (Excluding Reactor Programs), Sept. 1, 1975, to Feb. 29, 1976, ORNL/TM-5533 (July 1977).
8. S. D. Clinton and J. S. Watson, "Tritium Removal from Liquid Metals by Sorption on Yttrium," Proceedings of the Seventh Symposium on Engineering Problems of Fusion Research, CONF-771029-87, Vol. II, pp. 1647-49 (October 1977).
9. J. B. Talbot and F. W. Wiffen, "Recovery of Tritium from Solid Lithium-Sintered Aluminum Product (SAP) and Lithium-Aluminum Alloys," J. Inorg. Nucl. Chem. 41, 439-44 (1979).
10. R. F. Gould, ed., Separation of Hydrogen Isotopes, ACS Symposium Series 68, American Chemical Society, Washington, D.C., 1978.
11. O. N. Salmon, The Electrolytic Separation of Hydrogen Isotopes by Migration Through a Palladium Membrane, Knolls Atomic Power Laboratory, KAPL-1272 (June 25, 1976).
12. D. W. Ramey et al., "Tritium Enrichment from Aqueous Systems," presented at the Department of Energy, Division of Waste Management, Production, and Processing, Detritiation Meeting, Washington, D.C., Feb. 28-Mar. 1, 1978.

13. D. W. Ramey, Hydrogen Isotope Separation by Differential Permeation, M.S. Thesis, The University of Tennessee, Knoxville, March 1977.
14. D. W. Ramey et al., "Hydrogen Isotope Separation by Bipolar Electrolysis with Countercurrent Electrolyte Flow," presented at the Symposium on Separation Science and Technology Applications, Gatlinburg, Tenn., Oct. 30-Nov. 7, 1979.
15. D. W. Ramey, Solid State Division, ORNL, personal communication, error estimates.
16. R. E. Barker, Determination of Best Fit Data Within Material Balance Constraints Through the Least Squares Technique (to be published as an ORNL/TM report).
17. D. W. Ramey et al., Tritium Separation from Light and Heavy Water, ORNL-5581 (October 1979).

4. RESOURCE RECOVERY

The Resource Recovery program is concerned with the recovery of valuable minerals from energy-related waste streams, reduction of the environmental impact of solid-waste disposal through the recovery of toxic components, and recovery of minerals of importance to energy production from new or secondary ores. The program is supported by the DOE/Office of Basic Energy Sciences and currently focuses on fundamental studies of techniques for the recovery of metal values from fly ash. Other resource recovery problems and opportunities will be investigated as time and funds permit.

4.1 Recovery of Resource Materials from Coal Ashes

R. M. Canon, F. G. Seeley, W. J. McDowell,
K. B. Brown, and J. S. Watson

Laboratory scale testing of the Calsinter and $\text{NaCl}/\text{Na}_2\text{CO}_3$ processes for recovering mineral values from coal combustion fly ash continued. The Calsinter process,¹ originally designed to use CaSO_4 and CaCO_3 as sintering reagents, was shown to be effective when flue-gas desulfurization sludge (FGDS) is substituted for CaSO_4 , as shown in Fig. 4.1. No significant difference in aluminum recovery was observed at sintering temperatures above 1200°C when this substitution was made. Because FGDS is produced in about equal quantity with fly ash (at scrubber-equipped power plants), the concept of using the two solid wastes in one process is very attractive.

The behavior of other materials in the Calsinter sinter-leach steps was studied, and the degree to which several components were dissolved is shown in Fig 4.2. From 1000 to 1400°C , the dissolution of Fe, Ti, U, and

Fig. 4.1. Substitution of FDGS for CaSO_4 in the Calsinter process.

ORNL-DWG 78-12285

USING THE CALSINTER PROCESS, RECOVERIES
OF Fe, Ti, U, AND Mn (AS WELL AS Al)
INCREASE WITH INCREASING SINTERING
TEMPERATURE

Fig. 4.2. Effect of sintering temperature on the recovery of Al, Fe, Ti, Mn, and U by the Calsinter process.

Mg, like that of aluminum, increases with sintering temperature.

Preliminary dissolution tests were made of several trace elements designated by the Environmental Protection Agency as hazardous in drinking water. About 100% of the As, Cr, Cd, and Ag was dissolved, but lesser fractions of the Ba, Pb, Se, and Hg were dissolved. The leachability (hazard) of the remaining solid material was not evaluated.

Woth was initiated on developing the process steps required downstream of the acid leach. These steps include chemical separation of the materials dissolved in the leach step. Possibilities being investigated include solvent extraction of the iron from the aluminum and separation of iron and aluminum by continuous ion exchange.

Solvent extractions using 30% Primene JM-T in kerosene removed iron and titanium from a neutralized leach liquor; about 98% of the aluminum remained in the aqueous phase. This stream could have been processed to yield alumina. Alternatively, continuous ion exchange with an $(\text{NH}_4)_2\text{SO}_4$ - H_2SO_4 mixture and gradient elution techniques can be used to separate iron and aluminum. Other separations methods will be investigated in the future.

Additional studies were initiated to investigate recycle of H_2SO_4 in the Calsinter process and the use of Calsinter residue as an additive to cement.

Studies with the hydrolysis waste continued. The char from this process was burned at about 900°C to produce ash. Direct acid leach of this material with H_2SO_4 recovered more than 90% of the aluminum. Material from coal that had been pretreated with Na_2CO_3 showed no higher recovery rate than that from untreated coal (Table 4.1). The lower firing

Table 4.1. Aluminum recovery from hydrocarbonization char (Illinois #6 coal)

Coal pretreatment	Sintering agents	Leach agent	Aluminum leached (%)
None		4 <u>N</u> H ₂ SO ₄	86.9
None		8 <u>N</u> H ₂ SO ₄	94.5
Na ₂ CO ₃		4 <u>N</u> H ₂ SO ₄	93.3
Na ₂ CO ₃		4 <u>N</u> HNO ₃	94.4
Na ₂ CO ₃	FGDS	4 <u>N</u> H ₂ SO ₄	83.7
Na ₂ CO ₃	CaCO ₃ + FGDS	4 <u>N</u> H ₂ SO ₄	88.2

temperature must, therefore, be largely responsible for the ease with which this ash can be processed (in comparison to fly ash).

Investigations with gasifier ash, which contains less iron and aluminum than some of the fly ashes, began with attempts to recover metals with a direct leach. Preliminary results indicate that this is not effective. The Calsinter process, however, is effective, and lower reagent-to-ash ratios are required for the gasifier ash than for fly ash. Tests to determine the required ratio are in progress.

4.2 References for Section 4

1. R. M. Canon, F. G. Seeley, V. A. DeCarlo, W. J. McDowell, J. S. Watson, and K. B. Brown, "Removal and Recovery of Metals from Fly Ash," presented at the Conference on Ash Technology and Marketing, London, England, Oct. 22-27, 1978.

ORNL/TM-6647/V2
Category UC 13

INTERNAL DISTRIBUTION

1. Biology Library	45. A. D. Kelmers
2-3. Central Research Library	46. J. A. Klein
4. Document Reference Section	47. D. D. Lee
5-6. Laboratory Records	48. N. E. Lee
7. Laboratory Records - RC	49. R. E. Leuze
8. MIT Practice School	50. W. S. Lyon
9. ORNL Patent Section	51. A. P. Malinauskas
10. E. J. Arcuri	52. L. E. McNeese
11. S. I. Auerbach	53. O. B. Morgan
12. J. A. Auxier	54. J. E. Mrochek
13. R. E. Barker	55. E. Newman
14. J. M. Begovich	56. G. E. Oswald
15. J. T. Bell	57. W. W. Pitt
16. W. J. Boegly	58. B. R. Rodgers
17. W. D. Bostick	59. M. W. Rosenthal
18. C. R. Boston	60. D. D. Schuresko
19. J. I. Brand	61. S. W. Schwenterly
20. R. E. Brooksbank	62. C. D. Scott
21. C. H. Brown	63. F. G. Seeley
22. W. D. Burch	64. W. D. Shults
23. J. B. Cannon	65. S. E. Shumate
24. R. M. Canon	66. D. Steiner
25. R. S. Carlsmith	67. M. G. Stewart
26. S. D. Clinton	68. G. W. Strandberg
27. H. D. Cochran	69. J. B. Talbot
28. C. F. Coleman	70. T. Tamura
29. M. S. Denton	71. I. L. Thomas
30. S. R. Dinsmore	72. D. B. Trauger
31. B. Z. Egan	73. J. S. Watson
32. L. M. Ferris	74. J. R. Weir
33. P. W. Fisher	75. R. G. Wymer
34. W. Fulkerson	76. E. L. Youngblood
35. R. K. Genung	77. A. Zucker
36. T. M. Gilliam	78. L. Burnis, Jr. (consultant)
37. R. W. Glass	79. G. R. Choppin (consultant)
38. H. Goeller	80. W. H. Corcoran (consultant)
39. C. W. Hancher	
40. H. H. Haselton	
41. J. R. Hightower	
42. H. N. Hill	
43. R. L. Jolley	
44. O. L. Keller	

EXTERNAL DISTRIBUTION

81. J. L. Anderson, Los Alamos Scientific Laboratory, P. O. Box 1663,
Los Alamos, NM 97545
82. J. E. Baublitz, Office of Fusion Energy, DOE, Washington, D.C. 20545
83. J. E. Clarke, Office of Fusion Energy, DOE, Washington, D.C. 20545
84. F. E. Coffman, Office of Fusion Energy, DOE, Washington, D.C. 20545
85. R. P. Epple, Office of Basic Energy Sciences, DOE, Mail Station
J-309, GTN, Washington, D.C. 20545
86. W. Fedarko, Office of Fossil Energy, DOE, Washington, D.C. 20545
87. Dean Golden, Electric Power Research Institute, 3412 Hillview Avenue,
P. O. Box 10412, Palo Alto, CA 94303
88. W. J. Haubach, Office of Basic Energy Sciences, DOE, Mail Station
J-309, GTN, Washington, D.C. 20545
89. H. T. Jones, Office of Fossil Energy, DOE, Washington, D.C. 20545
90. E. E. Kintner, Office of Fusion Energy, DOE, Washington, D.C. 20545
91. M. R. Murphy, Office of Fusion Energy, DOE, Washington, D.C. 20545
92. F. G. Parker, TVA, 1320 Commerce Bank Bldg., Chattanooga, TN 37401
93. E. S. Pierce, Office of Basic Energy Sciences, DOE, Mail Station
J-309, GTN, Washington, D.C. 20545
94. M. Roberts, Office of Fusion Energy, DOE, Washington, D.C. 20545
95. F. Dee Stevenson, Office of Basic Energy Sciences, DOE, Mail Station
J-309, GTN, Washington, D.C. 20545
96. V. E. Weaver, Office of Fossil Energy, DOE, Washington, D.C. 20545
97. Office of Assistant Manager, Energy Research and Development,
DOE-ORO, Oak Ridge, TN 37830
- 98-124. Technical Information Center, Oak Ridge, TN 37830