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Semiannual Progress Report for
the Period April 1, 1977, to
September 30, 1977
Volume 2: Engineering
Science Programs**

MASTER

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CHEMICAL TECHNOLOGY DIVISION

ADVANCED TECHNOLOGY SECTION SEMI-ANNUAL PROGRESS REPORT
FOR THE PERIOD APRIL 1, 1977, TO SEPTEMBER 30, 1977
VOLUME 2: ENGINEERING SCIENCE PROGRAMS

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MASTER

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SUMMARY

Chemical Engineering Research

The annular continuous chromatograph has been significantly modified to effectively eliminate angular dispersions. This is an important improvement which was necessary for eventual applications of the device. Separations that had been evident from observations through the optically transparent chromatograph walls can now also be observed in the effluent streams. This capability provides an additional method for studying the performance of the device and permits study of separations that are not suitable for colorimetric analysis. Experimental studies included investigation of the capacity (maximum throughput) of the chromatograph for Co-Ni (cobalt-nickel) separation and studies of different separations on the device. An effective method for separating the major metals found in fly ash (aluminum and iron) was demonstrated, but lanthanide separation using citrate eluent was not effective on the continuous chromatograph because large sorbent volume changes disrupted the bed.

New correlations were developed for flooding rates and mass transfer rates with countercurrent flow of gases and liquids in columns filled with Goodloe wire-mesh packing. An investigation of hydroclones for removing solids from viscous liquids showed a significant decline in separation efficiencies as the viscosity was increased to 80 cP.

Studies of solid aggregation processes in coal-derived liquids showed that the presence of asphaltenes is important to aggregation of solids after addition of n-decane (antisolvent) to SRC (solvent refined coal) liquid. Quantitative measurements of the ζ potential of filtered solids

in oil (+13 mV) and asphaltenes in oil (-35 mV) suggest that electrical attraction between precipitated asphaltenes and the solid particles may account for the observed solid aggregation and high settling rates.

Fusion Energy

A new experimental apparatus was completed and used to study hydrogen pumping speeds with molecular sieve 5A at temperatures above 10 K. The new apparatus provides significant improvements in panel temperature measurements and temperature control. Eighty-two runs were made at different panel temperatures and gas feed rates. The pumping speed decrease with time was much like that observed in helium pumping on the 5A sieve at 4.2 K. The effects of mass transfer on pump speed were also evident in hysteresis curves produced when the panel was heated and cooled. The average pump speed over a few minutes generally declined with increasing panel temperature.

Studies of tritium sorption from liquid lithium onto yttrium metal were continued using the batch contact equipment; 28 runs were completed. Rapid sorption rates were observed during the first 2 hr and then declined, indicating that diffusion in the stagnant lithium was affecting or controlling the mass transfer rate. Further evidence of important resistance in the lithium, rather than yttrium, phase was obtained when the lithium was quickly withdrawn and replaced with fresh lithium. The sorption rate with fresh lithium returned to the high initial rate rather than the lower rate observed just before the original lithium was removed. Equilibrium sorption data can be obtained from the long-contact-time runs. The Sieverts constant (solubility) for tritium in yttrium was found to be

$$K_s \text{ (ppm/torr}^{\frac{1}{2}}\text{)} = 0.557 \exp (22,860/RT)$$

over the temperature range (250 to 400°C) and concentration range (25 to 30 ppm) studied. These values are close to extrapolations of results obtained by Yannopoulos with hydrogen at much higher temperatures (650 to 950°C) and higher concentrations (up to 0.1 m.f.).

The rates at which tritium is released from Li-Al (lithium-aluminum) and Li-SAP (sintered aluminum product) alloys were studied at temperatures from 350 to 500°C. The release rate could be described by diffusion within the solid alloy, and the diffusion coefficient for Li-SAP was found to be

$$D \text{ (cm}^2\text{/sec)} = 2.275 \times 10^{-4} \exp (-19,460/RT) .$$

The diffusion coefficient for Li-Al at 450°C was much higher than that for Li-SAP (more than three orders of magnitude). These diffusion coefficients are both high enough that the residual tritium inventory in a fusion reactor blanket would not prohibit the use of either material.

Resource Recovery

Laboratory-scale tests to develop methods for the recovery of resource materials from fly ash are continuing, and the studies have recently been expanded to include waste from ORNL studies of hydrolysis. Processes currently being investigated for fly ash include a series of sinter-leach processes. Of all the processes tested for fly ash, the Calsinter and NaCl/Na₂CO₃ sinter-leach processes are the most promising. In the Calsinter process, the fly ash is sintered with a CaSO₄•CaCO₃ mixture (perhaps utilizing flue gas desulfurization sludge) at ~1200°C and leached with 4 N sulfuric acid at reflux conditions. In the second

process, fly ash is sintered with a $\text{NaCl} \cdot \text{Na}_2\text{CO}_3$ mixture at 1000°C and leached with 1 N nitric acid. Both of these methods are capable of recovering >90% of the aluminum. Other sinter-leach processes using sulfate salts of Na, K, Mg, and Ca in various combinations with fly ash and sintering at 1000°C followed by a 1 N H_2SO_4 leach have been tested, but no other process has proved to be effective in extracting aluminum.

For the hydropyrolysis waste, a direct 4 N sulfuric or nitric acid leach at reflux conditions recovered >90% of the aluminum. The high recovery of aluminum with direct acid leach is noteworthy. Apparently the lower firing temperature and perhaps the fact that the coal had been preheated with Na_2CO_3 increase the reactivity of the ash by not forming refractory silica-alumina compounds. This may be true for ashes from other low-fired coal conversion processes.

Solvent extraction systems are being developed for use in these processes. Then, in addition to producing a high-purity Al_2O_3 product, a variety of other useful (or hazardous) minerals such as Fe, Ti, Mn, U, and Th can be removed and recovered from fly ash. Recent proposed solid waste regulations suggest that removal of several of these trace metals may significantly reduce the difficulty and cost of disposing of fly ash or any residual solid from the process. The Calsinter process has an additional attraction from an environmental point of view because it utilizes flue gas desulfurization sludge, which is a current and growing disposal problem.

1. INTRODUCTION

The Engineering Science Program in the Advanced Technology Section consists of three parts: (1) Chemical Engineering Research, (2) Fusion Energy, and (3) Resource Recovery. The Chemical Engineering Research studies and the Resource Recovery studies are supported by the U.S. Department of Energy (DOE)/Office of Basic Energy Sciences. The Fusion Energy studies are supported in part by the DOE/Office of Basic Energy Sciences and in part by the DOE/Office of Fusion Energy.

2. CHEMICAL ENGINEERING RESEARCH

The Chemical Engineering Research program includes several fundamental studies of chemical engineering problems that are important to energy development. These studies are funded by the DOE/Office of Basic Energy Sciences. Current activities are concerned with new equipment for chromatographic and absorption processes and with physical and chemical methods for separating solids from viscous liquids. These studies are of importance in coal conversion, nuclear fuel reprocessing, and a variety of separation processes.

2.1 Continuous Chromatography

R. M. Canon and W. G. Sisson

Investigation of the cobalt-nickel carbonate amine system, described previously,¹ has continued. Design improvements have been made to the chromatograph, and an entirely new bed support/exit assembly has been fabricated and installed (Fig. 2.1). This assembly consists of an ~36-cm-diam stainless steel plate with a V-groove machined to match the chromatograph annulus. Exit tubes are placed at 2° intervals (180 tubes) around the circumference flush with the groove surface, and a small porous Teflon insert is driven into each hole as a bed support. The resulting bed does not significantly promote circumferential mixing and yet allows collection of discrete samples from the chromatograph. Analyses of solutions from these exit tubes can now be used to accurately determine the separations achieved. A Perkin-Elmer spectrophotometer has been connected to a single exit tube to operate as an in-line instrument. As the reference (sample) tube rotates with the chromatograph bed,

ORNL DWG 77-2065

Fig. 2.1. Resin support/exit assembly for the continuous annular chromatograph.

the spectrophotometer produces a signal much like a standard chromatogram. Pressure drop through the porous Teflon is low, and measurements show that the flow rates through all exit tubes are equal (within 3%).

Tests have been made to determine the maximum feed rate possible for the cobalt-nickel separation. It is likely that the commercial leach liquor will be adjusted (with CO_2) to pH 7.8. This will precipitate some nickel (but no cobalt) and will result in a feed concentration of approximately 4 g/liter of nickel and 1 g/liter of cobalt. The continuous annular chromatograph (CAC) has been operated with a feed rate of $6.5 \text{ cm}^3/\text{min}$ at this feed composition with acceptable separation. The initial bandwidth for this limiting case was approximately 10° . Only one feed location was used, but three feed points would be possible. This would increase the total area of the initial bandwidth to 30° or 1/12 of the total chromatograph area. It would not be difficult to build a new device with a much larger diameter, perhaps 2.8 m (ten times that of the prototype). The annulus width could then be at least 14 cm (5% of the diameter). This would give a total feed area of 0.10 m^2 (1/12 of the total area). If the device were designed to operate at 1000 psi, the total flow velocity would be increased by a factor of 10 (to 0.24 m/min), and a suitable length would be about 2.0 m. The total feed rate to this device (using three feed locations) would then be about 1530 liters/hr. The resin volume would be 2.4 m^3 , and the eluent requirement, 16,500 liters/hr. Such a device would produce annually about 45,000 kg of nickel (<0.6 ppm cobalt) and 11,000 kg of cobalt (<3 ppm nickel). Larger devices could be built, but a unit of this size could produce high-purity cobalt or nickel in suitable quantities. Alternative methods of

operation which reduce cross-contamination further are available. These methods include operation at high pH (9.4) and use of gradient elution continuous chromatography. Work in these areas is continuing.

Investigations of the separation of praseodymium and neodymium have been conducted. These lanthanides were eluted using Dowex 50W-X8 ion exchange resin with citric acid as the eluent. The rare earths were introduced into the column as nitrates. When the resin was maintained in the citrate form, virtually no loading occurred and no separation was achieved. Variation of eluent rate, concentration, and sample size had no effect. However, when the resin was conditioned with 2 M HCl (changing the resin to the hydrogen form) prior to the run and then washed with H₂O, the rare earths were retained on the column. The rate of elution is a strong function of citrate concentration for these cases, but the separation was poor. Neither column length nor citrate concentration affected the separation. These observations led to the conclusion that displacement chromatography, not elution chromatography, was at work. Separation was unacceptable in all cases and work in this area has been terminated. The large sorbent volume changes common in displacement chromatography will, in general, make it unattractive for the continuous chromatograph. The CAC will function with multiple streams, but these severe disturbances to the sorbent bed cause serious operating problems.

Studies of the recovery of resource materials, specifically metals from fly ash, within the Engineering Science Program have produced an acid leach liquor containing aluminum and iron nitrates. These and other metals would be leached from fly ash with 8 M HNO₃, separated, and sold to the metals processing industries. Schemes have been developed² to

separate iron and aluminum using several concentrations of acid ranging up to 4 M; however, the gradient elution sequence for this method again results in unacceptable sorbent volume changes for the continuous chromatograph. In addition, the high free acid content of the leach liquor prevents it from loading on the ion exchange resin. However, evaporation of the liquor to dryness and redissolution of the solids with the stoichiometric amount of acid will produce a usable feed. This operation requires ~2.0 equivalents of acid per liter of leach liquor to completely dissolve the solids. Development of a chromatographic method for this separation will be pursued.

2.2 Packed Columns for Cryogenic Sorption Systems

J. M. Begovich

Goodloe packing, a knitted stainless steel wire-mesh packing, is being considered for use in cryogenic gas-liquid sorption systems for treatment of off-gas streams in nuclear fuel processing plants. To evaluate this packing, an experimental study of flooding rates and mass transfer characteristics in air-CO₂-water systems was reinitiated during this report period. Previous results were extended to include liquid-to-gas mass flow ratios up to two orders of magnitude larger than those studied previously.

2.2.1 Experimental apparatus

The experimental apparatus, consisting of three 100-cm-long columns with inside diameters of 6.35, 15.2, and 27.9 cm, and the procedures for obtaining flooding and mass transfer data have been described previously.³ A tracer technique⁴ was used to verify the assumption that the liquid

phase is in plug flow through the columns. A pulse of salt solution was injected into one liquid stream at the top of the column, and its residence-time distribution (RTD) was monitored at the column outlet using a conductivity probe and a strip-chart recorder.

2.2.2 Results

Flooding. Flooding data obtained in the 6.35- and 15.2-cm-ID columns using Goodloe packing⁵ are compared in Fig. 2.2 with previous results⁶⁻⁹ and with the Goodloe (packing manufacturer's) correlation.¹⁰ The coordinate axes correspond to a generalized flooding correlation for packed beds,¹¹ where

G = superficial gas mass flux ($\text{g cm}^{-2} \text{ sec}^{-1}$),

Ψ = ratio of water density to liquid density (dimensionless),

μ_L = liquid viscosity (cP),

g = gravitational constant (980 cm/sec^2),

ρ_G = gas density (g/cm^3),

ρ_L = liquid density (g/cm^3),

L = superficial liquid mass flux ($\text{g cm}^{-2} \text{ sec}^{-1}$).

The packing factor, F , has been omitted from the ordinate since its sole purpose is to force experimental flooding data for different packing shapes to fit the generalized correlation.

As can be seen in Fig. 2.2, results have been obtained for L/G ratios up to two orders of magnitude greater than those previously studied or reported by the packing manufacturer. For the high L/G ratios, the data appear to fall along an extension of the Goodloe correlation, while at lower ratios (<10) the data deviate significantly from the correlation. Since the data shown in Fig. 2.2 were obtained by several investigators,

Fig. 2.2. Comparison of flooding data obtained in Goodloe-packed columns.

the use of the dashed curve representing the experimental data is recommended in designing systems with this type of packing. For design purposes, a safety factor of approximately 30% is recommended to allow for scatter in the data.

Mass transfer. Peclet numbers for axial dispersion (based on the column length) were obtained for the 15.2-cm-ID column from the monitored RTD curves. The resulting values ranged from 11 to 26, indicating an intermediate amount of dispersion in the liquid phase. Thus the overall volumetric mass transfer coefficient $K_L a$ was calculated (1) by ignoring dispersion and assuming plug flow in the liquid phase and (2) by using an average value of 18 for the Peclet number in the solution to the dispersion equations given by Miyauchi and Vermeulen.¹²

The results of these calculations are given in Table 2.1. Since the difference between the two calculated coefficients is small and is within the experimental error, the value of $K_L a$ subsequently discussed will be that based on the plug flow model. Previous mass transfer results are given in Table 2.2, and both the new and previous data are plotted in Fig. 2.3 as a function of the superficial liquid mass flux. As the liquid mass flux was increased, $K_L a$ also increased approximately linearly. The effect of gas mass flux on $K_L a$ is difficult to determine, as shown in Fig. 2.4. The data are badly scattered and gas flow rates (for a single liquid rate) were not varied enough to establish the dependence of $K_L a$ on gas rates. However, numerous other investigators using the air-CO₂-water system in columns with other packing materials have found $K_L a$ to be independent of the gas flow rate.¹³ Thus, correlating all the $K_L a$ data given in Tables 2.1 and 2.2 as a function of only the liquid

Table 2.1. Mass transfer data of Ayala et al. (Ref. 5)

Liquid mass flux (g cm ⁻² sec ⁻¹)	Gas mass flux (g cm ⁻² sec ⁻¹)	Column diameter (cm)	$K_L a / pf$ (sec ⁻¹) ^a	$K_L a / d$ (sec ⁻¹) ^b
1.640	0.0162	15.2	0.03707	0.04080
0.809	0.0162	15.2	0.00698	0.00724
2.849	0.0045	15.2	0.06383	0.07067
3.530	0.0045	15.2	0.00292	0.00294
2.849	0.0070	15.2	0.04273	0.04565
2.018	0.0096	15.2	0.03272	0.03509
1.338	0.0265	15.2	0.01234	0.01284
0.970	0.0514	6.35	0.00158	0.00159
0.970	0.0303	6.35	0.02204	0.02466
2.331	0.0303	6.35	0.06683	0.07692
0.970	0.0062	6.35	0.01197	0.01275
1.488	0.0062	6.35	0.05248	0.06268
2.007	0.0062	6.35	0.02477	0.02640
2.526	0.0062	6.35	0.05284	0.05893
2.526	0.0135	6.35	0.07317	0.08461

^a $K_L a / pf$ is the mass transfer coefficient calculated on the basis of plug flow in the liquid phase.

^b $K_L a / d$ is the mass transfer coefficient calculated on the basis of the axial dispersion model.

Table 2.2. Mass transfer data of Chao et al. (Ref. 7)

Liquid mass flux (g cm ⁻² sec ⁻¹)	Gas mass flux (g cm ⁻² sec ⁻¹)	Column diameter (cm)	$K_L a / pf$ (sec ⁻¹)
0.139	0.0608	6.35	0.0038
0.278	0.0608	6.35	0.0074
0.486	0.0608	6.35	0.0104
0.625	0.0608	6.35	0.0130
0.379	0.0608	6.35	0.0029
0.379	0.0734	6.35	0.0036
0.379	0.0842	6.35	0.0033
0.379	0.0937	6.35	0.0038
0.0485	0.0435	15.2	0.0006
0.1091	0.0435	15.2	0.0011
0.4409	0.0435	15.2	0.0042
0.9920	0.0435	15.2	0.0091

Fig. 2.3. Effect of liquid flow rate on $K_L a$.

Fig. 2.4. Effect of gas flow rate on $K_L a$.

mass flux results in

$$K_L a / p_f = (0.014 \pm 0.002) L^{1.006 \pm 0.274}, \quad (1)$$

where the coefficients are given with their 95% confidence limits.

Equation (1) is plotted in Fig. 2.3.

2.2.3 Future work

No future work is currently planned in this area. It is felt that use of the experimental curve in Fig. 2.2 and Eq. (1) will yield accurate estimates of the flooding rates and mass transfer characteristics, respectively, for Goodloe packed columns operating under conditions similar to those used in this study.

2.3 Hydraulic Cyclone Studies

J. B. Talbot

Experiments to evaluate the performance of a 10-mm-diam hydroclone were continued during this reporting period. Hydroclones are potentially useful devices for the removal of solids from coal liquids, but their ability to separate micron-sized particles from relatively viscous liquids has not been adequately tested. Performance criteria are usually defined by pressure drop, the ratio of the underflow rate to the overflow rate, and cyclone efficiency, which is dependent on the physical properties of the solids and liquid medium.

2.3.1 Experimental procedures

The apparatus and procedures used to study hydroclones have been described previously.¹⁴ Slurry from a stirred tank is recirculated by a

pump through a 10-mm Dorr-Oliver hydroclone. The inlet, overflow, and underflow streams are sampled for each pressure drop, and particle size distributions are determined using a ZB Coulter Counter with a model H4 Channelyzer. Samples of the overflow and underflow are dried and weighed to determine solids concentration. Some minor alterations in the system and procedure have been made to improve the accuracy of the results. The pressure gages at the inlet and outlets of the hydroclone were repositioned to be as close to the hydroclone openings as possible. The procedure to determine solids concentration in the overflow and underflow samples was also modified. The liquid from the 10-ml aliquots is evaporated for about 4 hr on a hot plate at 400°C. Then the samples are dried further in an oven at 500°C. This technique has improved the material balances; errors are now less than 5%.

During this reporting period, experiments have been conducted using slurries containing ~5 wt % kaolin in water-glycerin solutions with viscosities of 1, 3.75, and 7 cP. The kaolin particles (sp gr, 2.40 g/cm³) are less than 10 μ in diameter (approximately 70 wt % of the particles are less than 5 μ in diameter).

2.3.2 Results

Experiments were begun to determine the effects of flow rate and viscosity (below 30 cP) on both pressure drop and hydroclone efficiency. Figure 2.5 is a comparison of the feed-to-overflow pressure drop vs feed rate at 1, 3.75, and 7 cP. The data from each viscosity were fit to an equation of the form

$$\Delta P = aQ^b ,$$

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Fig. 2.5. Pressure drop vs feed capacity.

where

ΔP = feed-to-overflow pressure drop (psi),

Q = feed rate (gpm),

a, b = constant coefficients selected by the regression analysis,
and the coefficients are listed in Table 2.3.

Table 2.3. Coefficients for $\Delta P = aQ^b$ curves
for kaolin-glycerol solutions

Viscosity (cP)	a	b	Coefficient of determination, r^2
1	79.76	1.953	0.9928
3.75	63.62	2.095	0.9959
7	58.03	1.841	0.9928

The data at 1 and 3.75 cP agree with a relationship in the literature¹⁴ which states that the pressure drop is proportional to the square of the feed rate. The crossover of the 7-cP curve is similar to results obtained previously at even higher viscosities.¹⁵ This crossover occurs in a series of runs with varying pressure drops when the ratio of underflow-to-overflow rate falls below unity. At low viscosities the underflow-to-overflow rate ratio remains larger than one.

Hydroclone efficiency is affected by an increase in viscosity. Figure 2.6 shows that the gross efficiency, the ratio of the solids discharge rate at the underflow to the total solids feed rate, decreases at higher viscosities. A comparison of the gross efficiency (at a feed

Fig. 2.6. Effect of viscosity on gross efficiency.

rate of 0.5 gpm) vs viscosity for AC Test Dust, fly ash, and kaolin is also shown in Fig. 2.6.

Point efficiencies were determined for the data taken at 1 cP. Point efficiency expresses the centrifugal efficiency for a given size particle which is removed through the underflow, and centrifugal efficiency is defined as follows:

$$E = \left(\frac{G - R_f}{1 - R_f} \right),$$

where G is gross efficiency and R_f is the ratio of underflow to feed flow rate. Point efficiencies were calculated from the size analyses, solids content, and flow rates of both overflow and underflow streams.¹⁶ Of course, the same information can be obtained from the composition and flow rate of the feed and either the overflow or underflow rate, but the data for the overflow and underflow streams were used in this study. An error analysis¹⁷ indicated that the best accuracy in both total (gross) efficiency and point efficiency was obtained from measurements made on these streams. Figures 2.7 and 2.8 show point efficiency as a function of particle diameter for feed rates (Q) of 0.62 and 1.04 gpm, respectively. The data show the trend of the expected S-shaped curves, which had not been seen in previous data.¹⁵ However, the particle size analyses were not extended to diameters $>3 \mu$. This will be corrected in future particle size determinations as other viscosities are studied.

The effect of solids content on the viscosity of the kaolin-glycerol solutions was also determined, since correlations in the literature indicate that either liquid viscosity or viscosity of the total solution may

Fig. 2.7. Point efficiencies for kaolin in l-cP solution
(Q = 0.62 gpm).

Fig. 2.8. Point efficiencies for kaolin in 1-cP solution

(Q = 1.04 gpm).

be used in correlations of hydroclone performance. The results are tabulated in Table 2.4. Solids concentration has a pronounced effect on the viscosity of the mixture.

Table 2.4. Effect of solids content on the viscosity of kaolin-water and kaolin-glycerol mixtures

Weight percent solids	Viscosity (cP) ^a
<u>Kaolin-water</u>	
0	0.99
1.98	1.30
4.97	1.57
9.20	2.41
<u>Kaolin-glycerol</u>	
0	6.50
2.00	6.83
5.00	7.82
10.0	14.26

^aAt 23.2°C for kaolin-water mixture and at 23.6°C for kaolin-glycerol mixture.

2.4 Fundamental Agglomeration Studies in Heavy Organic Media

B. R. Rodgers and J. D. Hewitt

2.4.1 Introduction

The tendency for particles to agglomerate and precipitate, or to disperse and stabilize, is characterized by a number of physical parameters,¹⁸⁻²⁰ the most obvious of which are size and density relative to the suspending matrix. Generally, colloidal dispersions are defined as those dispersed particles with diameters $<1\ \mu\text{m}$, an artificial limit corresponding roughly to the maximum size 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 former particles are not difficult to remove by conventional techniques, but the remaining dispersed particles often constitute up to 50 vol % of the total particle mass²¹ and must be removed to meet stringent EPA specifications.

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 with electrolytes or surface-active agents. Even though the agglomerated condition represents the lowest thermodynamic energy state, an energy barrier must exist which prevents particle adhesion on contact. Thus the rate of agglomeration depends on the collision frequency of 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 close approach of particles must also be lowered, or little agglomeration will occur. Verwey and Overbeek¹⁸ have shown that energy barriers can be caused by overlapping double layers that interact to increase the free energy of the system, thus leading 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 electrical double layer, often can be related to the agglomerating tendency of the dispersion. Kitahara,^{19,22} among others, has extended the above theory to nonaqueous (low-electrolyte) systems. This project has applied the theory to coal-derived liquids by showing that significant zeta potentials indeed do exist for particles in the liquefaction product. Also, components that are precipitated by aromatics (carbenes and carboids) and components that are precipitated by paraffins (asphaltenes) are shown to have zeta potentials of two to three times those of unconverted particles.

2.4.2 Theory

The principal theory for electric double layers was formulated independently by Derjaguin and Landau²³ and Verwey and Overbeek¹⁸ during the forties and is generally referred to as the DLVO theory. This theory is generally accepted as the basic theory for stability of lyophobic colloids. According to the DLVO theory, the interaction between colloidal particles is controlled by electrostatic repulsion due to the double layer and attraction due to van der Waals forces. However, the theory is not adequate for describing the stability of polymer and polyelectrolyte

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,²⁴ heptane,²⁵ and toluene,²⁶ iron oxide and alumina in xylene,²⁷ etc. Some conductivity was imparted to these solutions by the addition of organic-soluble dissolution compounds such as calcium oleate, Aerosol OT, calcium di-isopropyl salicylate, etc.; no zeta potential was measured in the absence of electrolyte.

The theory as developed is confusing to many scientists because the original development occurred when the electrostatic (or Gaussian) system was popular. Consequently, the theory is based on Gaussian units (g.u.) — cm, g, sec, electrostatic units (e.s.u.), and statvolt — some of which are seldom encountered. Adding to the confusion, a number of other unit systems have frequently been used in the literature, some of which are the Heavyside-Lorentz (h.l.u.), pure electrostatic units (e.s.u.), electromagnetic units (e.m.u.), and practical units (pr.u.). Often equations are given in mixed units, and extensive use of conversion factors is necessary. To avoid confusion, a derivation is given below which is self-consistent and oriented toward engineers.

The basic fundamental equations on which the development depends are given in items 1 to 8 below.

1. Coulomb's law (inverse square law). Two charges a distance, r , apart exert a force on each other which is proportional to their charge and inversely proportional to their distance of separation,

$$F = \delta \frac{qq'}{r^2}, \quad (1)$$

where δ is the proportionality factor, q is the charge (as yet undefined), and r is the distance (unit must be defined). The manner in which δ is defined in this equation affects the form of all subsequent equations. In g.u., δ was defined to be one and unitless, so that

$$F = \frac{qq'}{r^2} \quad (2)$$

in a vacuum. Here, F is in dynes and r is in centimeters. This defines the charge as follows: 1 e.s.u. is in the point charge that will produce a force of 1 dyne on an equal charge 1 cm away. If the charges are in a dielectric medium, this equation must be modified such that

$$F = \frac{qq'}{Dr^2}, \quad (3)$$

where

$$D = \text{dielectric constant} = \frac{\epsilon}{\epsilon_0} = \frac{\text{permittivity in medium}}{\text{permittivity in vacuum}}.$$

As before, $\epsilon_0 = 1$ in g.u.

Equation (1) is defined in pr.u. (m, kg, sec, volt, coul) as

$$F = \frac{1}{4\pi\epsilon_0} \frac{qq'}{r^2}$$

for a vacuum, or

$$F = \frac{1}{4\pi\epsilon} \frac{qq'}{r^2} \quad (4)$$

for a dielectric medium. The permittivity in a vacuum, ϵ_0 , equals $8.854 (10^{-12}) \text{ sec}^2/\text{m}^2$ for this system. The two equations can be shown to

be equivalent by substituting values in the proper units. However, e.s.u., coulomb, statvolt, and volt are derived units and can be expressed in basic units as follows:

$$1 \text{ e.s.u.} = 1 \frac{\text{cm}^{3/2} \text{ g}^{1/2}}{\text{sec}},$$

$$1 \text{ coulomb} = 1 \text{ m}^{1/2} \text{ kg}^{1/2},$$

$$1 \text{ statvolt} = \frac{\text{g}^{1/2} \text{ cm}^{1/2}}{\text{sec}},$$

$$1 \text{ volt} = \frac{\text{kg}^{1/2} \text{ m}^{3/2}}{\text{sec}^2}.$$

Once these definitions are established, the other equations follow in a consistent manner for a given set of units.

2. Gauss' theorem. The electric flux through a closed surface is proportional to the charge contained within the surface:

$$\phi = \left(\frac{1}{\epsilon} \right) q \text{ (in pr.u.)} \quad (5)$$

or

$$\phi = \frac{4\pi}{\epsilon} q \text{ (in g.u.)} \quad (6)$$

Equations in the practical units have been "rationalized"; that is, the factor 4π has been eliminated from subsequent equations by the choice of the constant in Coulomb's law. (The 4π arises naturally in the derivation of Gauss' law.) Because of this simplification and the widespread use of Scientific International (SI) units (which define ampere rather than

coulomb as a basic unit), only the practical system of units will be used for the remainder of the derivation.

3. Definition of electric field. The proportionality constant between a charge and the force it experiences is defined as

$$\underline{F} = \underline{E} q . \quad (7)$$

Using this definition, the flux can be written

$$\phi = \iint_S \underline{n} \cdot \underline{E} dS , \quad (8)$$

and Gauss' law can be upgraded to

$$\epsilon \iint \underline{n} \cdot \underline{E} dS = Q , \quad (9)$$

where Q is the total charge within a Gaussian surface.

4. Definition of electric potential. The proportionality constant between a charge and the work required to move it from point 1 to point 2 is

$$W_{12} = V_{12} q . \quad (10)$$

This work may also be represented as the force times the distance moved, or

$$W_{12} = - \oint \underline{F} \cdot d\underline{l} ,$$

and since $\underline{F} = \underline{E} q$,

$$W_{12} = - \oint q \underline{E} \cdot d\underline{l} = V_{12} q .$$

By differentiation, the potential is related to the electric field,

$$\underline{E} = -\underline{\nabla} V_{12} . \quad (11)$$

The minus sign arises because the force is the reaction force which keeps the particle from accelerating during its travel from point 1 to point 2 (reversible work).

5. Poisson's equation. This equation, the starting point for most electrokinetic phenomena, relates the surface potential of a particle to the charge density surrounding the particle and the permittivity of the medium. Total charge is

$$Q = \iiint_V \rho \, dV, \quad (12)$$

where charge density $\rho = \text{coulombs/m}^3$. Using Gauss' divergence theorem,

$$\iint_S \underline{n} \cdot \underline{F}(x, y, z) dS = \iiint_V \underline{\nabla} \cdot \underline{F}(x, y, z) dV,$$

to convert the flux in Eq. (9) to a volume integral and substituting Eq. (12) for the total charge gives

$$\iiint_V \underline{\nabla} \cdot \underline{E} \, dV = \iiint_V \frac{\rho}{\epsilon} \, dV$$

or

$$\underline{\nabla} \cdot \underline{E} = \frac{\rho}{\epsilon}. \quad (13)$$

Substituting Eq. (11) gives Poisson's equation,

$$\nabla^2 V_{12} = -\frac{\rho}{\epsilon}. \quad (14)$$

(Note: in g.u., this is $\nabla^2 V_{12} = -\frac{4\pi\rho}{\epsilon}$.)

6. Derivation of the general double-layer equation. Assume that a double layer such as that illustrated in Fig. 2.9 exists on the solid surface and that there is a slipping plane somewhere in the diffuse

Fig. 2.9. The electric double-layer for a particle with a radius much greater than the double-layer thickness.

region. The approach is to make a momentum balance on an arbitrary volume in the diffuse layer, as shown in Fig. 2.9.

Total change of momentum for the volume element	=	Net change of momentum due to the sum of all forces acting on the surface	+	Net change of momentum due to flow through the surface by convection and conduction	+	Net change of momentum due to external forces on elements throughout the volume
--	---	--	---	--	---	--

Momentum by surface action due to pressure forces = P

Momentum by convection due to flow of fluid = $\rho \underline{v} \underline{v}$

Momentum by conduction due to viscous forces = $\underline{\tau}$

Momentum by volume action due to gravity forces = $\rho \underline{g}$

Momentum by volume action due to electrical forces = $\rho_c \underline{E}$

Momentum generated by a moving surface = $\rho \underline{v} \underline{v}_s$

Thus,

$$\begin{aligned} \frac{d}{dt} \iiint_V \rho \underline{v} dV = & - \iint_S \underline{n} \cdot \rho \underline{v} \underline{v} dS + \iint_S \underline{n} \cdot \rho \underline{v} \underline{v}_s dS - \iint_S \underline{n} \cdot \underline{\tau} dS \\ & - \iint_S \underline{n} P dS + \iiint_V \rho \underline{g} dV + \iiint_V \rho_c \underline{E} dV . \end{aligned} \quad (15)$$

Using Liebnitz's formula for differentiation of a triple integral,

$$\frac{d}{dt} \iiint F(x, y, z) dV = \iiint_V \frac{\partial F(x, y, z)}{\partial t} dV + \iint_S \underline{n} \cdot F(x, y, z) \underline{v}_s dS , \quad (16)$$

and Gauss' divergence theorem,

$$\iint_S \underline{n} \cdot F(x, y, z) \underline{v} dS = \iiint_V \underline{\nabla} \cdot F(x, y, z) \underline{v} dV , \quad (17)$$

Eq. (15) becomes

$$\iiint_V \left(\frac{\partial \rho \underline{v}}{\partial t} + \underline{\nabla} \cdot \rho \underline{v} \underline{v} + \underline{\nabla} \cdot \underline{\tau} + \underline{\nabla} P - \rho \underline{g} - \rho_c \underline{E} \right) dV = 0$$

or

$$\frac{\partial \rho v}{\partial t} = -\underline{\nabla} \cdot \rho \underline{v} \underline{v} - \underline{\nabla} \cdot \underline{\tau} - \underline{\nabla} P + \rho \underline{g} + \rho_c \underline{E} . \quad (18)$$

For the present experiments, this equation must be simplified by assumptions that may not be justified in all cases (even though the assumptions are traditional).

7. Simplification of the general double-layer equation. The general double-layer equation [Eq. (18)] may be simplified as follows:

<u>Assumption</u>	<u>Eliminate</u>	<u>Justification</u>
1. Steady state	$\frac{\partial \rho v}{\partial t}$	No change in momentum with time
	$\underline{\nabla} \cdot \rho \underline{v} \underline{v}$	Convection in = convection out
2. Stationary liquid and particles move by electrophoresis	$\underline{\nabla} P$	Sum of pressure forces = 0
3. The volume is small and gravity is the same at all points	$\rho \underline{g}$	Negligible change in gravitational field within the volume

Allowing for the above,

$$\underline{\nabla} \cdot \underline{\tau} = \rho_c \underline{E} . \quad (19)$$

If the flow of particles is unidirectional (as in electrophoresis) and the electric field is tangential,

$$\frac{d \tau_{y,x}}{dy} = \rho_c E_t .$$

Substituting Newton's law,

$$\tau_{y,x} = -\mu \frac{dv_x}{dy} ,$$

gives

$$\mu \frac{d^2 v_x}{dy^2} + \rho_c E_t = 0 . \quad (20)$$

8. Derivation of zeta potential. The zeta potential equation is derived by eliminating a quantity that cannot be easily measured, the charge density, between Eqs. (14) and (20),

$$\frac{\mu}{E} \frac{d^2 v_x}{dy^2} = -\rho_c = \epsilon \frac{d^2 V_{12}}{dy^2} . \quad (21)$$

Assuming that μ , E , and ϵ are constant and integrating

$$\mu \int_0^\infty \frac{d}{dy} \left(\frac{dv_x}{dy} \right) dy = E\epsilon \int_0^\infty \frac{d}{dy} \left(\frac{dV_{12}}{dy} \right) dy$$

and

$$\mu \frac{dv_x}{dy} = E \epsilon \frac{dV_{12}}{dy} + C_1 ,$$

C_1 is evaluated by the boundary conditions. Since

$$\frac{dv_x}{dy} \Big|_\infty = \frac{dV_{12}}{dy} \Big|_\infty = 0 ,$$

$$C_1 = 0 .$$

A second integration yields

$$\mu v_x = E \epsilon V_{12} + C_2 .$$

Similarly,

$$v_x \Big|_\infty = v_{12} \Big|_\infty = 0 ,$$

since the liquid is assumed stationary in electrophoresis. Then,

$$V_{12} = \frac{\mu v_x}{\epsilon E} \quad (22)$$

One further assumption that was implicit in the development of Eq. (22) should be discussed. The double-layer thickness was assumed to be $\ll a$, the particle diameter; so the flat plane model shown in Fig. 2.10 could be used. When this assumption is not valid, Henry²⁸ shows that Eq. (22) should contain a factor which depends on the double-layer thickness and which varies from 1 for a thin double-layer to 1.5 for a very diffuse double-layer. The relationship of particle diameter to double-layer thickness for particles in coal-derived liquids is not known. However, some insight can be gleaned from an analysis of the particular conditions of the electrophoresis studies which are described below. First, in nonaqueous systems of low dielectric constant (~ 2), the ionic concentrations are very low and the diffuse layer would be very spread out, a fact which suggests use of the 1.5 factor. However, the particle size in these experiments was 5–20 μm which, due to this relatively large size, would support Eq. (22) as derived. Until further data can be obtained, Eq. (22) will be used to calculate zeta potentials from electrophoretic velocities in the experiments that follow.

2.4.3 Experimental

The liquefied coal was obtained from the Solvent Refined Coal (SRC) pilot plant at Wilsonville, Alabama, which is operated by Catalytic, Incorporated, for Southern Services and DOE. The sample was taken from the process line just prior to the filtration section and thus still

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Fig. 2.10. Microelectrophoresis slides. (a) Narrow groove;

(b) open window.

contained process-derived solvent. The coal for this particular run was an Illinois No. 6. An analysis of the material is given in ref. 29.

The liquefied coal was separated into four components using a procedure similar to that developed by Mima, Schultz, and McKinstry.³⁰ This fractionation is shown in Table 2.5.

Table 2.5. Fractionation of coal liquids

Component	Method of removal
1. Solids	Precoat filtration at 530°F
2. Carbenes and carboids	Soxhlet extraction with benzene (insoluble portion)
3. Asphaltenes	Soxhlet extraction of recovered extract from step 2 with pentane (insoluble portion)
4. Oils and resins	Recovered portion (solvent-free) from step 3

The asphaltenes obtained had a light brown, grainy amorphous appearance and had to be stored under a nitrogen blanket because they had a tendency to oxidize. The oils and resins obtained by these procedures can best be described as a clear, medium-yellow liquid when observed as a thin film at 450X magnification.

The 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 with a film thickness of ~ 50 μm [see Fig. 2.10(a)]. 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 slide was connected to a model D6 Oregon Electronics Regulated Power Voltage Supply and to the stage of a Series 10 Microstar Laboratory Microscope. Observations were at 40X and 100X; higher magnifications would have been desirable for the smaller particles, but the focal length of the microscope system at higher magnifications was too short for the sandwich slide system shown in Fig. 2.10(a). A different design [Fig. 2.10(b)] will be used to measure the electrophoretic velocity of smaller particles.

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 a time. Alternating electrode polarity and short time measurements were used to minimize these effects.

2.4.4 Results

When paraffins such as n-decane,³¹ kerosine,³² and other solvents^{33,34} are added to coal-derived liquids containing undissolved particles from the original coal, a thick precipitate forms rapidly. However, little is known about the mechanism of agglomeration. It has been suggested that coagulation and/or flocculation of certain species that are precipitated by paraffins act as collectors for the solid particles.^{29,35} To determine which components of coal liquids were causing the agglomeration, n-decane was sequentially added to oils and resins, asphaltenes,

carbenes and carboids, solids, and combinations of these. The results shown in Table 2.6 strongly indicate that asphaltenes are a necessary component for agglomeration. The function of carbenes and carboids will be determined at a future date.

Table 2.6. Effect of n-decane on coal-liquid components

Component	Observations at 450X in a 150- μ m film
1. Oils and resins	Medium-yellow solution
2. Oils and resins + 30% <u>n</u> -C ₁₀	Light-yellow solution (no solids)
3. Oils, resins, and asphaltenes	Medium-orange solution (no solids apparent)
4. Oils, resins, and asphaltenes + 30% <u>n</u> -C ₁₀	Medium-orange solution + stringy precipitate (dark yellow to reddish brown)
5. Oils, resins, and solids	Yellow solution, black dispersed particles (more spherical than asphaltenes)
6. Oils, resins, and solids + 30% <u>n</u> -C ₁₀	Solids remained dispersed
7. Oils, resins, asphaltenes, and solids + 30% <u>n</u> -C ₁₀	Solids agglomerated

Micrographs of the dispersed particles in solution 6 above and the agglomerated particles in solution 7 are shown in Figs. 2.11 and 2.12.

Although asphaltenes appeared to be semicrystalline long-chain particles, it was not clear whether agglomeration was aided by electrostatic effects or occurred entirely by flocculation mechanisms (long-chain bridging). To examine the possibility of electric charge effects,

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SCALE - MICRONS

0 100 200

Fig. 2.11. SRC oils and resins with filtered solids and
30% n-decane.

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SCALE - MICRONS

0 20 40

Fig. 2.12. SRC oils, resins, and asphaltenes with filtered solids and 30% n-decane.

electrophoretic velocities were determined by procedures outlined previously. These velocities were related to particle charge by

$$\zeta = \frac{\mu V_E}{E\epsilon}, \quad (23)$$

where

μ = viscosity (kg/m•sec),

V_E = electrophoretic velocity (m/sec),

E = electric field strength (V/m),

ϵ = permittivity of medium = dielectric constant x permittivity in a vacuum ($8.854 \times 10^{-12} \text{ sec}^2/\text{m}^2$).

To use Eq. (23), the viscosities, densities, and dielectric constants of the solutions were determined and are listed in Table 2.7. The viscosities were determined at 26°C with a Cannon-Fenske reverse-flow viscometer, the densities were determined with a standard pycnometer, and the dielectric constants were measured at 26°C in a Balsbough LRC-1 liquid reference cell. In the latter case, the reference cell was connected to a General Radio Capacitance Bridge Type 716-CS1 with bridge oscillator type 1330-A; measurements were made at a frequency of 1 Mc. A permanently fixed arrangement of electrical components was used to eliminate lead capacitances. Improved accuracy was obtained by using cyclohexane as liquid reference and calculating the dielectric constants from the following equation:³⁶

$$D_x - D_a = (C_x - C_a) \frac{D_s - D_a}{C_s - C_a}, \quad (24)$$

where C is capacitance (pF) and the subscripts refer to air (a), standard (s), and unknown solution (x).

Table 2.7. Physical properties of coal-derived solutions

Solution	Density (g/cm ³)	Viscosity (cP)	Dielectric constant
Oils and resins	0.986	5.97	4.00
Oils, resins, and asphaltenes	1.020	11.9	4.55
Oils, resins, asphaltenes, carbenes, and carboids	1.056	15.9	4.55

Obviously, densities vary only slightly, but the effects of coal asphaltenes on both viscosity and dielectric constant are marked. The viscosity increase lends some credence to the supposition that asphaltenes are a colloidal solution, and the increase in dielectric constant indicates that electrical charges are associated with asphaltenes. The dielectric constant of asphaltenes can be estimated by a technique given in ref. 37,

$$D = D_o \left[1 - (3) \frac{D_o - D_1}{2D_o + D_1} c \right],$$

where

D = dielectric constant of the solution,

D_o = dielectric constant of the liquid,

D_1 = dielectric constant of the solid,

c = concentration of particles, by volume.

If one assumes that asphaltenes are a colloidal solution in oils and resins,

$$4.55 = 4.00 \left[1 - (3) \frac{4.00 - D_1}{8.00 + D_1} (0.057) \right] ,$$

then D (asphaltenes) is ~54.9.

The addition of carbenes and carboids to a solution of oils, resins, and asphaltenes did not cause further change in the dielectric constant, indicating that these materials have dielectric constants similar to those of the previous solution.

The zeta potentials for various solutions can now be calculated from the electrophoretic velocity measurements. The results are shown in Table 2.8.

2.4.5 Discussion of results

The results in Table 2.8 show the charges on the various particles that can exist in coal liquids. The unexpected result is that the asphaltenes carry a negative charge (petroleum asphaltenes have generally been reported to have a positive charge). The asphaltenes, which had been separated and stored under nitrogen, were crushed with a mortar and pestle before addition to the oils and resins. It is speculated that some oxidation may have occurred during this process, which caused the surfaces to become negatively charged. Twenty percent n-decane was added to the solution to see if freshly precipitated asphaltenes had a similar negative charge; in this case the particle motion was toward the negative electrode, indicating a positive charge. The concentration after precipitation was too high to measure individual particle zeta potentials. Another indication that asphaltenes carry a positive charge while in solution is given by a dark-orange color concentration at the cathode

Table 2.8. Zeta potentials of coal-derived solids in coal-derived liquids from the SRC process

Solution	Number of particles measured	ζ (V)	Standard deviation (V)
Oils and resins		Base solution	
Oils, resins, and asphaltenes	13	-0.035	0.003
Oils, resins, carbenes, and carboids	14	+0.025	0.007
Oils, resins, and solids	23	+0.013	0.003
Oils, resins, asphaltenes, and solids			
Solids	18	+0.0074	0.0009
Asphaltenes	3	-0.013	0.002
Filtered oil and solids	11	+0.013	0.001

during electrophoresis. This observation also supports the theory that asphaltenes exist as a colloidal solution.

Other observations of interest from Table 2.8 are discussed below.

1. The presence of asphaltenes, carbenes, and carboids in these experiments did not change the zeta potential of the unconverted coal solids; that is, the value was the same in oils and resins as it was in filtered oil. The zeta potential was sufficiently high to maintain dispersion in both cases. At first this would seem to support the supposition that the adsorption of asphaltenes on the solid particle surface was not responsible for dispersion of unconverted coal particles. However, it should be remembered that the solids were filtered from the coal-derived oil, which contained asphaltenes, and that some adsorbed asphaltenes could have been removed with the solids.
2. The reconstituted mixture of asphaltenes and solids in oils and resins shows reduced zeta potentials and some agglomeration. Thus, it appears that asphaltenes neutralized some of the particle surface charge and allowed agglomeration due to the reduced double-layer repulsion at the lower potential.

Conductivities of the various solutions were measured to determine if asphaltenes are the charge-carrying species in coal-derived liquids. Table 2.9 shows that, while conductivity does increase with asphaltene addition, the major charge-carrying species are still present in oils and resins. Addition of solids lowers the conductivity slightly. The average standard deviation of the procedure was 0.09×10^{-7} mho/m.

Table 2.9. Conductivities of coal-derived liquids

Mixture	Conductivity at 21°C $\left(\frac{\text{mho}}{\text{m}} \times 10^7\right)$
Oils and resins	4.17
Oils, resins, and asphaltenes	6.44
Filtered oil	6.73
Unfiltered oil	5.25

The following mechanism for agglomeration of coal-derived particles is supported by these experiments: asphaltenes exist as a colloidal solution in coal-derived liquids and carry a significant positive charge. These positively charged asphaltenes are attracted to the mineral matter and unconverted coal which remains after coal liquefaction; a double-layer of positive charge is produced which contributes significantly to their stabilization. When solvents are added, which render the asphaltenes insoluble, they agglomerate rapidly and entrap the coal particles.

2.4.6 Conclusions

The following conclusions may be reached from these experiments:

1. Coal-derived particles have a significant zeta potential, indicating that electric charge contributes to their stability in coal-derived liquids.
2. Asphaltenes have a significant zeta potential and may act as particle stabilizers in coal-derived liquids.

3. Coal-derived particles do not agglomerate upon the addition of paraffins to coal-derived liquids that do not contain asphaltenes, carbenes, or carboids.
4. Asphaltenes agglomerate upon the addition of paraffins to coal-derived liquids; coal-derived particles are removed with the agglomerates.
5. Asphaltenes are a sufficient component for the agglomeration and removal of coal-derived particles by the addition of paraffins to coal-derived liquids.

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3. FUSION ENERGY

The efforts of the Chemical Technology Division in fusion energy are closely coordinated with those of the ORNL Fusion Energy Division and include the areas of fuel handling, processing, and containment. Current studies are concerned largely with the development of vacuum pumps for fusion reactors and experiments and with development and evaluation of techniques for recovering tritium from solid or liquid breeding blankets. In addition, a small effort is devoted to support of the ORNL design of a major Tokamak experiment, The Next Step (TNS). The more fundamental studies of blanket recovery processes are supported by DOE/Office of Basic Energy Sciences, and the remaining, more applied studies are supported by DOE/Office of Fusion Energy.

3.1 Cryosorption Vacuum Pumping

P. W. Fisher

During the past six months, the cryosorption vacuum pumping program initiated experiments designed to determine the best combination of adsorbent and operating temperature for near-term neutral beam injector systems. Vacuum pumps for these systems will have to accommodate only hydrogen at pressures near 10^{-4} torr during beam pulses. Although cryocondensation pumps are used in all present beam lines, cryosorption pumps have advantages that could make them attractive for use in future systems. These advantages include higher operating temperature, the ability to take larger heat loads, less sensitivity of pumping speed to small fluctuations in panel temperature, and the easier control of regeneration rates.

3.1.1 Experimental

The experimental apparatus used in these studies has four basic parts: a variable-temperature cryostat, cryosorption panel, chevron, and test chamber. Initial experiments were made with a 10-cm-diam cryosorption panel coated with molecular sieve 5A (MS-5A) prepared by the Excalibur Corporation. The panel was mounted on an Andonian cryostat. The temperature of the panel was regulated by adjusting the rate at which liquid helium drops fell to the back of the panel and by controlling the power supplied to a heater attached to the back of the panel. The temperature of the panel was measured with a thermocouple made of Chromel-gold with 0.07 at. % iron; the thermocouple was attached to the center of the front side of the panel. The liquid-nitrogen-cooled chevron assembly completely surrounded the cryosorption panel. The chevrons, which were 90° and just optically dense, covered the entire 6-in.-diam opening leading from the vacuum test chamber to the cryosorption panel. The vacuum test chamber was identical to that employed in all previous experiments. Additional details of the experimental apparatus have been presented in a previous report.¹

Tests were preceded by a 24-hr bake-out of the system at 200°C. During bake-out the entire vacuum system and cryosorption panel were evacuated by a set of liquid-nitrogen-cooled sorption roughing (VacSorb) pumps. After baking, the system was isolated from the roughing pumps and opened to a triode ion pump. The system was then completely isolated just prior to addition of liquid nitrogen to the chevron. Between each series of runs, the system was reactivated by warming it to room temperature and evacuating it with the sorption roughing pumps, followed by use

of the triode pump. The pressure of the warm system prior to cooling was approximately 10^{-6} torr.

Each run lasted 5 min, with 10 min allowed between runs. Performing tests at specific leak rates for specific times permits quick direct comparisons of results, especially comparison of the effects of panel temperature and type of adsorbent. During the 10-min recovery period, the panel was taken through various temperature cycles in order to promote mass transfer from the surface to the bulk of the adsorbent. These cycles involved heating the panel to either 40 or 60 K and returning it to the desired operating temperature. However, between some runs the panel temperature was maintained constant. Pumping speeds reported here were measured with a nude gage mounted ~ 9 in. in front of the chevron. Speeds have not been corrected for conductance restriction between the gage and chevron.

3.1.2 Results and discussion

Eighty-two runs in nine series were made with various panel temperatures, panel heating cycles between runs, and hydrogen feed rates. The time-averaged surface temperature, speed, and pressure for each 5-min run are shown in Table 3.1. The panel temperature could be held essentially constant for most runs; the only exceptions were those made at the highest feed rate (8.5×10^{-2} torr-liter/sec). During those runs the temperature rose steadily. During all runs the temperature at the center of the chevron was observed to be between 120 and 140 K, and the temperature at the bottom of the copper radiation shield was ~ 130 K. Plots of average pump speeds vs reciprocal panel temperature were prepared for

Table 3.1. Time-averaged temperature, speed, and pressure for 5-min runs

Run	Feed rate (torr-liters/sec)	Quantity accumulated during run (torr-liters)	Quantity accumulated prior to run (torr-liters)	Average surface temperature (K)	Average speed (liters/sec)	Average pressure (torr)	Thermal treatment prior to run ^a
A-1	8.2 E-5	0.02	0.00	15.3	614	1.4 E-7	R
2	8.2 E-5	0.02	0.02	15.3	710	1.2 E-7	H-60
3	8.2 E-5	0.02	0.05	15.1	803	1.1 E-7	H-60
B-1	8.2 E-5	0.02	0.00	14.2	553	1.6 E-7	R
2	6.7 E-4	0.20	0.02	14.3	217	5.6 E-6	C
3	5.6 E-3	1.68	0.23	15.0	31	2.2 E-4	C
4	8.5 E-2	27.03	1.91	26.7 ^b	21	4.1 E-3	C
C-1	8.2 E-5	0.02	0.00	30.3	33	4.0 E-6	R
2	6.7 E-4	0.20	0.02	30.3	23	3.3 E-5	C
3	5.6 E-3	1.68	0.23	30.3	14	4.0 E-4	C
4	8.5 E-2	25.50	1.91	25.5	20	4.3 E-3	C
5	5.6 E-3	1.68	27.41	35.4	15	4.6 E-4	H-40
6	5.6 E-3	1.68	29.09	30.2	18	3.7 E-4	H-40
7	5.6 E-3	1.68	30.77	25.4	22	2.9 E-4	H-40
8	5.6 E-3	1.68	32.45	21.1	60	2.0 E-4	H-40
9	5.6 E-3	1.68	34.13	15.2	175	1.3 E-4	H-40
10	5.6 E-3	1.68	35.81	12.1	492	1.8 E-5	H-40
D-1	8.2 E-5	0.02	0.00	12.4	674	1.2 E-7	R
2	6.7 E-4	0.20	0.02	12.6	466	1.9 E-6	C
3	5.6 E-3	1.68	0.23	12.6	218	2.6 E-5	C
4	8.5 E-2	25.50	1.91	13.2	464	1.8 E-4	C
5	5.6 E-3	1.68	27.41	12.6	196	2.9 E-5	C
6	5.6 E-3	1.68	29.09	12.3	244	2.4 E-5	H-40
7	5.6 E-3	1.68	30.77	15.1	182	3.7 E-5	H-40
8	5.6 E-3	1.68	32.45	20.3	31	2.4 E-4	H-40
9	5.6 E-3	1.68	34.13	25.1	21	3.4 E-4	H-40
10	5.6 E-3	1.68	35.81	31.8	13	4.5 E-4	H-40
11	5.6 E-3	1.68	37.49	36.0	10	5.8 E-4	H-40
12	8.5 E-2	25.50	39.17	36.7	16	5.3 E-3	H-40
13	8.5 E-2	25.50	64.67	32.4	18	4.7 E-3	H-40

Table 3.1 (continued)

Run	Feed rate (torr-liters/sec)	Quantity accumulated during run (torr-liters)	Quantity accumulated prior to run (torr-liters)	Average surface temperature (K)	Average speed (liters/sec)	Average pressure (torr)	Thermal treatment prior to run ^a
14	8.5 E-2	25.50	90.17	30.8 ^b	19	4.6 E-3	H-40
15	8.5 E-2	25.50	115.67	29.7 ^b	19	4.5 E-3	H-40
16	8.5 E-2	25.50	141.17	29.2 ^b	18	5.0 E-3	H-40
E-1	3.2 E-5	0.02	0.00	19.7	292	3.6 E-7	R
2	6.7 E-4	0.20	0.02	19.7	99	1.3 E-5	C
3	5.6 E-3	1.68	0.23	20.0	40	2.5 E-4	C
4	8.5 E-2	20.60	1.91	31.1 ^b	21	4.2 E-3	C
5	5.6 E-3	1.68	32.51	20.0	27	2.5 E-4	C
6	5.6 E-3	1.68	34.19	19.5	29	2.3 E-4	H-40
7	3.0 E-2	9.00	35.87	12.8	487	6.7 E-5	H-40
8	3.0 E-2	9.00	44.87	19.6 ^b	26	1.4 E-3	H-40
9	3.0 E-2	9.00	53.87	14.7	198	1.6 E-4	H-40
10	3.0 E-2	9.00	52.87	20.3	26	1.4 E-3	H-40
11	3.0 E-2	9.00	71.37	25.7	18	1.7 E-3	H-40
12	3.0 E-2	9.00	86.87	30.2	15	2.0 E-3	H-40
13	3.0 E-2	9.00	89.87	34.8	12	2.6 E-3	H-40
F-1	8.2 E-5	0.02	0.00	15.1	558	1.6 E-7	R
2	8.2 E-5	0.02	0.02	15.1	273	3.9 E-7	C
3	8.2 E-5	0.02	0.05	15.1	205	5.3 E-7	C
4	8.2 E-5	0.02	0.07	15.1	556	1.6 E-7	H-40
5	8.2 E-5	0.02	0.10	15.1	559	1.6 E-7	H-40
6	8.2 E-5	0.02	0.12	15.2	539	1.7 E-7	H-40
7	8.2 E-5	0.02	0.15	12.8	713	1.2 E-7	H-40
8	6.7 E-4	0.20	0.20	12.8	382	2.7 E-6	C
9	5.6 E-3	1.68	0.37	12.8	206	3.0 E-4	C
10	8.5 E-2	25.5	2.05	13.3	858	1. E-4	C
11	6.7 E-4	0.20	27.55	12.6	465	2.4 E-6	H-40
12	6.7 E-4	0.20	27.75	24.8	28	2.8 E-5	H-40
13	6.7 E-4	0.20	27.96	20.4	73	1.6 E-5	H-40
14	6.7 E-4	0.20	28.16	33.9	15	4.6 E-5	H-40
15	6.7 E-4	0.20	28.36	30.2	18	3.9 E-5	H-40

Table 3.1 (continued)

Run	Feed rate (torr-liters/sec)	Quantity accumulated during run (torr-liters)	Quantity accumulated prior to run (torr-liters)	Average surface temperature (K)	Average speed (liters/sec)	Average pressure (torr)	Thermal treatment prior to run ^a
G-1	8.2 E-5	0.02	0.00	15.1	509	1.7 E-7	R
2	8.2 E-5	0.02	0.02	15.0	498	1.8 E-7	H-40
3	8.2 E-5	0.02	0.05	15.0	489	1.8 E-7	H-40
4	8.2 E-5	0.02	0.07	15.2	499	1.8 E-7	H-60
5	8.2 E-5	0.02	0.10	14.9	536	1.6 E-7	H-60
6	8.2 E-5	0.02	0.12	15.0	534	1.6 E-7	H-60
7	8.2 E-5	0.02	0.15	25.2	29	4.0 E-6	H-40
8	8.2 E-5	0.02	0.17	12.8	661	1.3 E-7	H-40
9	8.2 E-5	0.02	0.20	28.4	17	5.9 E-6	H-40
10	8.2 E-5	0.02	0.22	18.9	163	9.3 E-7	H-40
11	8.2 E-5	0.02	0.25	33.5	11	7.7 E-6	H-40
H-1	8.2 E-5	0.02	0.	15.1	486	1.8 E-7	R
2	8.2 E-5	0.02	0.02	15.0	523	1.7 E-6	H-60
3	8.2 E-5	0.02	0.05	15.0	554	1.6 E-7	H-60
4	8.2 E-5	0.02	0.07	15.0	543	1.6 E-7	H-60
5	8.2 E-5	0.02 ^c	0.10	15.0	512	1.7 E-7	H-40
I-1	8.2 E-5	0.02	0.00	15.1	581	1.6 E-7	R
2	8.4 E-5 ^d	0.03	0.02	15.1	213	5.2 E-7	H-40
3	8.4 E-5 ^d	0.03	0.05	15.1	82	1.5 E-6	C
4	8.4 E-5 ^d	0.03	0.08	15.1	66	1.7 E-5	C
5	8.4 E-5 ^d	0.03 ^c	0.10	15.1	214	5.0 E-7	H-40

^aR = cooled from room temperature; C = temperature held constant at previous operating temperature between runs; H-40 = panel heated to 40 K and recooled to operating temperature prior to run; and H-60 = panel heated to 60 K and recooled to operating temperature prior to run.

^bTemperature fluctuated more than ± 0.5 K during run.

^cRun was longer than 5 min; average values for first 5 min are shown.

^dLeak valve broke prior to run and was recalibrated after run; however, the setting may have changed in transit.

each specific feed rate (Q); see Figs. 3.1–3.5. Only runs preceded by heating cycles are presented in these plots. For most feed rates, the curves are approximately linear over the entire temperature range studied. The maximum pumping speed observed for hydrogen using the 10-cm-diam MS-5A panel in this pump was ~ 825 liters/sec. At the lowest feed rate (8.2×10^{-5} torr-liter/sec, Fig. 3.1), the speed approached this value with decreasing temperature. Average test chamber pressures are plotted in Fig. 3.6 as a function of reciprocal panel temperature for all feed rates studied. Cross plots of average speed vs feed rate and average speed vs average pressure are presented in Figs. 3.7 and 3.8, respectively. A comparison of similar curves for various cryosorption panels will allow us to choose the best adsorbent for hydrogen pumping. For the sorbent material (MS-5A) used in these initial tests, it appears that the best pumping speeds are obtained at the lowest temperatures.

Pumping speeds are plotted as a function of hydrogen accumulation in Figs. 3.9 and 3.10 for two different feed rates and three different sorbent panel temperatures. At the low feed rate, the speed is substantially higher than the time-averaged speed for about 30% of the test period. However, at the higher feed rates the speed remains more nearly steady and only slightly less than the average for $\sim 95\%$ of the test period. Fluctuations shown in the middle curve in Fig. 3.10 are correlated directly with slight variations in surface temperature (± 0.3 K) which result from actions of the temperature controller.

Although comparison of speeds recorded over specific time increments simplifies the experimental procedure and makes for ease in comparison of results, it is not an exact test and may lead to some misconceptions about

Fig. 3.1. Average speed as a function of panel temperature for 5-min runs made after heating panel to 40 or 60 K.

Fig. 3.2. Average speed as a function of panel temperature for 5-min runs made after heating panel to 40 or 60 K.

Fig. 3.3. Average speed as a function of panel temperature for 5-min runs made after heating panel to 40 or 60 K.

Fig. 3.4. Average speed as a function of panel temperature for 5-min runs made after heating panel to 40 or 60 K.

Fig. 3.5. Average speed as a function of panel temperature for 5-min runs made after heating panel to 40 or 60 K.

Fig. 3.6. Average pressure as a function of temperature for 5-min runs made after heating panel to 40 or 60 K.

Fig. 3.7. Average speed as a function of feed rate at various temperatures. Data were taken from the curves plotted in Figs. 3.1-3.5.

Fig. 3.8. Average speed as a function of average pressure.

Data were taken from the curves plotted in Figs. 3.1-3.6.

Fig. 3.9. Pumping speed as a function of hydrogen accumulation at the lowest feed rate tested. Panel was heated to 40 or 60 K prior to each of these runs.

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Fig. 3.10. Pumping speed as a function of hydrogen accumulation at the highest feed rate for which the panel temperature could be held constant during the run. Panel was heated to 40 K prior to each of these runs.

the steady-state behavior of the pump. Figure 3.11 shows pumping speed as a function of accumulation for three runs at different feed rates with the panel temperature at ~ 15 K. The accumulation at the end of a 5-min run is shown for each curve. The accumulation after a fixed time is inversely proportional to the leak rate. Comparison of the average speeds for such runs shows that on this basis the lowest feed rate (run H5) gave the highest 5-min speed; the 5-min speeds for runs D7 and E9 were approximately equal. However, continuation of run H5 to longer times shows that the speed drops off significantly after 5 min. If the speeds were compared at the steady-state values rather than over a specific time interval, the lowest feed rate would give the lowest speeds. Somewhat similar behavior has been observed during helium pumping with the Excalibur pump.¹

Six of the nine series of runs were started with the same feed rate (8.2×10^{-5} torr-liter/sec) and panel temperature (~ 15 K). The average speeds for these runs are plotted in Fig. 3.12. Although there is scatter in the data, there appears to be no trend. This indicates that, at least for this number of regenerations studied, there was no detectable degradation in speed as a result of regeneration.

Figures 3.13 and 3.14 show the pressure response of the closed system (pump and test chamber with no leak) to two different temperature cycles. These tests were made between pumping runs. The first cycle was to 40 K, and the latter cycle was to 60 K. Several experiments of this type were made, and these figures are representative of nearly identical observations. Both curves show wide hysteresis loops. As the temperature was raised from ~ 15 K (where the last experiment was performed) to ~ 30 K, the pressure in the pump and test chamber rose as hydrogen was released from

Fig. 3.11. Pumping speed as a function of hydrogen accumulation for three feed rates at ~ 15 K. Panel heated to 40 K prior to each run.

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Fig. 3.12. Average speed for first run in each series in which the panel temperature was ~ 15 K.

Fig. 3.13. System pressure as a function of temperature for a 40 K temperature cycle between runs H-4 and H-5.

Fig. 3.14. System pressure as a function of temperature for a 60 K temperature cycle between runs H-3 and H-4.

the panel; but as the temperature was increased further (to ~ 40 K), the pressure decreased, indicating hydrogen was resorbed on the panel. Apparently, material adsorbed at 15 K is adsorbed only in surface micropores of the MS-5A. As the panel is heated, the equilibrium pressure of this material rises. However, at the same time, the diffusivity of hydrogen in the sieve also increases, and at ~ 30 K mass transfer rates between surface micropores and the bulk of the MS-5A become significant. When this occurs, the surface pores become depleted, and the panel again begins to pump hydrogen. If the temperature is increased still further, as shown in Fig. 3.14, the pressure will again begin to increase as equilibrium sorption conditions for the bulk of the adsorbent become less favorable. Finally, if the temperature is decreased, the pressure also decreases, reaching much lower values, which are more indicative of clear surface micropores. Previous data following warming and cooling curves in the Excalibur pump¹ showed a plateau pressure of $\sim 10^{-4}$ torr and a temperature between 20 and 40 K, much like the horizontal portion of the heating curves of Figs. 3.13 and 3.14. The experimental cooling curves shown in Figs. 3.13 and 3.14 with equilibrium adsorption isotherms are in good agreement with equilibrium sorption isotherms at temperatures above 50 K.

Figure 3.15 shows the effects of different heat treatments between consecutive runs. Heating the panel to 40 K led to slight decreases in speed in the next run, whereas heating to 60 K generally (but not always) led to increases in speed. Apparently, heating the panel to 60 K is only slightly better than heating to 40 K. The remarkable increases in speed observed in the first series of runs (A) could be due to the relatively slow cooling rate used prior to this run (1 hr to go from 150 K to

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Fig. 3.15. Average pumping speeds for consecutive runs in indicated series at the lowest feed rate and ~ 15 K. Panel temperature programs were different prior to some series and between runs.

15 K). In all other series of runs, except for series H, the panel was cooled in less than 15 min. The cooling rate in series H was very slow, requiring 2 hr to go from 150 K to 15 K. For series H, increased pumping speed was observed during the first three runs; however, the speed increases were small when compared with those of series A. Unusual effects observed in series A could be due to adsorption on very active sites, possibly inside sodalite units. Such sites, when filled, are not easily reactivated, that is, are not reactivated at room temperature.

When the panel is not heated between runs, the speed decreases with each succeeding run, as indicated by the first three runs in series F (Fig. 3.15). These three runs along with run H5, which is an extended run at the same feed rate and temperature, are shown in detail in Fig. 3.16. At the end of each short run, the speed approaches the pumping speed for continuous pumping. However, for a substantial period of time at the beginning of a run, the pump speeds are much higher. This ability to pump for short periods at high speeds is encouraging for the application of cryosorption pumps to neutral beam injector systems because these systems are pulsed and the effective speeds may be much greater than the steady-state speeds. These pumps will receive gas on a very short duty cycle. The 150-kV beams for the Tokamak Fusion Test Reactor (TFTR) are expected to pulse for 0.5 sec every 90 sec. Therefore, the pumps have 180 times the pulse length to recover from the pulse.

3.1.3 Program status

The demountable cryosorption pump is in the process of being reconstructed with a panel coated with type Na-Y molecular sieve. At the same

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Fig. 3.16. Comparison of pumping speeds (as a function of hydrogen accumulation) for three consecutive runs without intermediate panel warming and for a continuous run at the same feed rate and temperature.

time, the chevron is being changed from stainless steel to copper to provide better thermal protection for the panel. Other modifications to the liquid helium distribution system behind the panel are also being made with the intent of getting better cryogen utilization and reaching lower temperatures. Pumping speed tests are expected to resume shortly.

3.2 Tritium Sorption from Liquid Metals

S. D. Clinton and J. S. Watson

3.2.1 Introduction

Molten lithium appears to be the most promising blanket material for breeding tritium in fusion reactors. One of the techniques being considered for the recovery of tritium from liquid lithium is sorption by a hydrogen-gettering metal. Tritium sorption from molten lithium and potassium (potential blanket coolant) has been studied in a batch contactor at temperatures of 250 to 400°C using metal sorbent samples of yttrium and zirconium. Yttrium has shown significant removal rates from both molten lithium and potassium; however, the sorption rates from potassium appear to be too slow for a practical recovery process. At 300°C, an yttrium sample reduced the concentration of tritium in lithium by a factor of 2 in 24 min, whereas the half-life of tritiated lithium in contact with a similar yttrium sample at 400°C was ~50 min. At the higher temperature, the lower sorption rate may be due to a reduced concentration driving force. Although the data are not complete, the results to date demonstrate the feasibility of such a blanket-recovery system.

3.2.2 Experimental equipment

A schematic diagram of the equipment used to contact tritiated liquid metals with selected metal sorbents has been published.² The equipment consists of a liquid metal reservoir containing dissolved tritium, two sampling valves, two isolated contacting chambers (volume, $\sim 20 \text{ cm}^3$ each), a vacuum source, and an argon supply. The tritiated lithium can be drawn into the two contacting chambers at a temperature between 200 and 400°C. One chamber contains the metal sorbent, and the second chamber serves as a control. To terminate an experiment, the two lithium samples are removed from the contactor chambers, dissolved in water, and analyzed for tritium by liquid scintillation counting.^{3,4} To reduce the problem of oxygen contamination, the entire process is enclosed in a glove box with a once-through flow of dry argon. The glove box operates at a slightly negative pressure, exhausting to a radioactive off-gas system, and therefore serves as secondary containment to protect personnel from tritium.

3.2.3 Results and discussion

Twenty-eight batch contactor runs were conducted with tritiated lithium and a single yttrium metal sample obtained from Research Chemicals (Division of Nucor Corporation). The metal sample dimensions were 0.31 by 1.39 by 3.73 cm (geometric surface area of 13.5 cm^2), and the weight was 3.55 g. The first 19 sorption runs (see Table 3.2) were made at 400°C with contact times ranging from 5 min to 100 hr. An additional 9 runs (see Table 3.3) were conducted at temperatures from 250 to 400°C and contact times of 120 to 360 hr to determine equilibrium concentrations. A lithium control sample was removed with each sorption run to confirm

Table 3.2. Results of the tritiated lithium-yttrium sorption experiments at 400°C

Run No.	Contact time (hr)	Tritium concentration in lithium		Ratio of C to C ₀
		Sorber, C (ppb)	Control, C ₀ (ppb)	
1	24	149	785	0.19
2	75	102	794	0.13
3	48	114	793	0.14
4	16	96	791	0.12
5	8	134	790	0.17
6	4	182	778	0.23
7	1	376	778	0.48
8	100	94	780	0.12
9	2	332	780	0.43
10	1	390	767	0.51
11	0.5	535	776	0.69
12	0.25	608	766	0.79
13	0.17	664	774	0.86
14	0.08	685	735	0.93
15	0.75	556	768	0.72
16	3	270	755	0.36
17	3	307	771	0.40
18	3	285	730	0.39
19	30	152	726	0.21

Table 3.3. Results of the tritiated lithium-yttrium equilibrium sorption experiments

Run No.	Temperature (°C)	Contact time (hr)	Sorber, C (ppb)	Control, C _o (ppb)	Yttrium, C _y (ppm)
20	400	120	126	728	19.0
21	350	120	73	703	20.6
22	300	120	56	740	22.3
23	250	120	34	727	23.9
24	300	360	33	718	25.4
25	350	240	72	746	26.7
26	300	240	28	730	28.2
27	400	287	148	753	29.3
28	250	314	10	713	30.9

the initial concentration of tritium in the lithium. From the 28 control analyses, the average tritium concentration in the lithium feed reservoir was 757 ± 27 ppb.

The results of the first 23 tritium sorption experiments are shown in Fig. 3.17, where the concentration of tritium remaining in the lithium, C , divided by the initial tritium concentration, C_0 , is plotted as a function of the contact time. Runs 1 through 20 were conducted at 400°C , whereas runs 21, 22, and 23 were at respective temperatures of 350, 300, and 250°C . The sorption rate data at 400°C are comparable to the data obtained at 300°C ;¹ however, the concentration driving force is significantly reduced at the higher temperature. For contact times less than 1 hr at 400°C , the tritium concentration in the lithium decreased as a first-order reaction with a half-life of ~ 50 min. For increasing times greater than 1 hr, the tritium sorption rate decreased slowly and appeared to approach zero for contact times in the order of 100 hr. The slightly lower mass transfer rate observed in run 1 is in agreement with the initial runs using tritiated potassium and lithium at 300°C .^{1,2} Apparently, the yttrium surface requires a certain amount of time to become activated. The apparent rate decrease in runs 19 and 20 can be attributed to a reduced concentration driving force due to tritium accumulation in the yttrium sample. Comparing runs 2 and 20, the bulk tritium concentration in the yttrium sample increased from 2.4 to 19 ppm.

Runs 11, 12, 13, and 14 (respective contact times of 30, 15, 10, and 5 min) were used to calculate a mass transfer coefficient of $(2.7 \pm 0.4) \times 10^{-4}$ cm/sec. In this calculation, it is assumed that the driving force was the tritium concentration in the lithium; the ratio of yttrium surface

Fig. 3.17. Normalized tritium concentration in lithium as a function of contact time for yttrium sorber experiments.

area to lithium volume for the four runs was $0.89 \pm 0.08 \text{ cm}^{-1}$. The magnitude of the mass transfer coefficient for a natural-convection system suggests that the controlling mass transfer resistance may be in the lithium phase; however, the value is a factor of 2 smaller than the coefficient determined similarly at 300°C .¹ Subsequent yttrium-tritium equilibrium measurements permitted the tritium concentration driving force in the lithium to be reduced; however, the liquid-film mass transfer coefficient was increased only 10% ($3.0 \times 10^{-4} \text{ cm/sec}$).

The results of runs 17 and 18 substantiate speculation that the controlling mass transfer resistance is in the lithium phase. A minimum time period of 24 hr was maintained between all of the remaining runs to eliminate any existing tritium concentration gradient in the yttrium sample. Only 14 min separated the termination of run 17 and the beginning of run 18. After 3-hr contact times, the normalized tritium concentrations remaining in the lithium were 0.40 and 0.39, respectively, for runs 17 and 18. These data suggest that tritium sorption is not inhibited by tritium diffusion in the yttrium for contact times in the order of 3 hr.

Runs 20 through 23 were conducted at contact times of 120 hr to determine equilibrium conditions for the tritiated lithium-yttrium system. The temperature of the four runs was decreased from 400 to 250°C in 50° increments. Although subsequent data indicated that the tritium concentrations were changing, the results in Fig. 3.17 illustrate the effect of temperature. The normalized tritium concentrations remaining in the lithium were 0.17, 0.10, 0.076, and 0.047 for respective temperatures of 400, 350, 300, and 250°C . During the four consecutive runs (20 to 23),

the tritium concentration in the yttrium, C_Y , increased from 19.0 to 23.9 ppm (see Table 3.3).

An additional five runs, 24 to 28, were conducted at increased contact times (240 to 360 hr) in an attempt to attain equilibrium (see Table 3.3). Comparing runs 24 and 26 at respective contact times of 360 and 240 hr, the tritium concentration in the lithium appears to be independent of time. The data from these five runs were used to establish the tritium solubility in yttrium as a function of temperature.

Smith et al.⁵ have measured the solubility of tritium in lithium as a function of temperature (700 to 1000°C) and pressure (0.1 to 760 torr). For tritium mole fractions less than 0.1, the temperature dependence of solubility is given by the following equation:

$$K_S = 42.8 e^{10,104/RT} , \quad (1)$$

where K_S is the Sieverts' law constant (ppm/torr^{1/2}), R is the gas constant (1.987 cal/g-mole·K), and T is temperature. Extrapolating Eq. (1) to lower temperatures, Sieverts' law constants, $K_S(\text{LiT})$, were calculated for lithium-tritium (see Table 3.4). At equilibrium, the tritium partial pressures in the lithium and yttrium are equal; therefore, the Sieverts' constant, $K_S(\text{YT})$, for yttrium-tritium can be calculated by the following equation:

$$K_S(\text{YT}) = \frac{C_Y}{C_{\text{Li}}} K_S(\text{LiT}) , \quad (2)$$

where C_Y is the tritium concentration in yttrium (ppm) and C_{Li} is the tritium concentration in lithium (ppm). The Sieverts' law constants for

Table 3.4. Determination of the Sieverts' law constant as a function of temperature for yttrium-tritium

Run No.	Temperature (°C)	C _{Li} (ppm)	C _Y (ppm)	Equation (1), K _S (LiT) (ppm/torr ^{1/2})	Equation (2), K _S (YT) (ppm/torr ^{1/2})
24	300	0.033	25.4	3.06 x 10 ⁵	2.36 x 10 ⁸
25	350	0.072	26.7	1.50 x 10 ⁵	5.56 x 10 ⁷
26	300	0.028	28.2	3.06 x 10 ⁵	3.08 x 10 ⁸
27	400	0.148	29.3	8.18 x 10 ⁴	1.62 x 10 ⁷
28	250	0.010	30.9	7.15 x 10 ⁵	2.21 x 10 ⁹

yttrium-tritium are tabulated in Table 3.4 and plotted as a function of temperature in Fig. 3.18. The equation for the least-squares line in Fig. 3.18 is:

$$K_S = 0.557 e^{22,860/RT} \quad (3)$$

Yannopoulos, Edwards, and Wahlbeck⁶ have reported experimental isotherms for the yttrium-hydrogen system at temperatures from 650 to 950°C. For hydrogen mole fractions less than 0.1, a least-squares fit of the data (seven determinations) yields the following temperature dependence for hydrogen solubility in yttrium:

$$K_S = 0.80 e^{21,300/RT} \quad (4)$$

Compared to Eq. (3), the Sieverts' law constants predicted by Eq. (4) at temperatures from 250 to 400°C are low by a factor of 3; however, considering the temperature extrapolation and isotope effect, the agreement between the two solubility expressions is considered excellent.

Using Eqs. (1) and (3) for Sieverts' law constants and the tritium-yttrium concentrations, C_Y , in runs 20 to 23, Eq. (2) was used to calculate equilibrium values for C_{Li} . The calculated and experimental tritium in lithium concentrations (ppb) are tabulated in Table 3.5. In each of the four runs with a contact time of 120 hr, the experimental tritium in lithium concentration was greater than the calculated value by 20 to 33 ppb. Although the concentration data of runs 20 to 23 appeared to be unchanging with time (see Fig. 3.17), the consistent difference (25 ± 6 ppb) between experimental and calculated tritium-lithium concentrations justifies a 240-hr contact time to approach equilibrium.

Fig. 3.18. Variation of the Sieverts' law constant with temperature for the yttrium-tritium system.

Table 3.5. Comparison of calculated-equilibrium and experimental concentrations of tritium in lithium for 120-hr contact times

Run No.	Temp. (°C)	Equation (3) $K_S(YT)$ (ppm/torr ^{1/2})	Exp. C_Y (ppm)	Calc. C_{Li} (ppb)	Exp. C_{Li} (ppb)	Exp.-calc. ΔC_{Li} (ppb)
20	400	1.48×10^7	19.0	105	126	21
21	350	5.83×10^7	20.6	53	73	20
22	300	2.92×10^8	22.3	23	56	33
23	250	1.99×10^9	23.9	9	34	25

At the end of run 28, the yttrium metal sample was analyzed for tritium content by dissolving the metal in dilute hydrochloric acid and counting the resulting solution in a liquid scintillation spectrometer. On removal from the contactor chamber, the bulk of the yttrium sample appeared to be unchanged by the extended contact time with molten lithium; however, the bottom 20% of the yttrium stuck to the chamber walls and fractured into smaller pieces. The fractured yttrium pieces were recovered from the chamber by dissolving the solidified lithium (0.4 g) with water. A water rinse of the unfractured yttrium (2.84 g) prior to acid dissolution indicated that only 0.2 g of lithium had adhered to the intact yttrium surface. The total tritium recovered from the water dissolutions was 0.0010 Ci. From the lithium control and sorber samples during the 28 sorption experiments, the estimated tritium accumulation in the yttrium was 0.93 Ci (27.1 ppm). The tritium recovered from acid dissolution of the yttrium was 1.06 Ci (114% of the estimated amount), indicating a tritium concentration in the sorber sample of 30.9 ppm ($\sim T_{0.0009}$). The error in a tritium concentration analysis is ± 5 to 10%. Lithium sampling losses between runs (~ 0.6 g) could cause the estimated tritium accumulation in the yttrium to be low by $\sim 10\%$.

3.2.4 Program status

Sorption on a hydrogen-gettering metal appears to be one of the more promising techniques for the recovery of tritium from liquid lithium. Although the studies are not complete, the results to date demonstrate the feasibility of such a blanket-recovery process system. During the next six months, the batch contactor system will be used to tritiate

several yttrium coupons for subsequent regeneration experiments. An electromagnetic pump and flow meter have been ordered for use in a forced-convection tritium sorption experiment to be assembled during the next report period.

3.3 Tritium Recovery from Solid Li-Al and SAP Blanket Materials

J. B. Talbot

Several lithium alloys and compounds have been suggested as potential breeding materials for fusion reactors.⁷ The main advantages of solid blankets are that the structural and breeding materials do not acquire long-lived radioactivity under blanket conditions and there is the possibility of achieving a system with a low tritium inventory. However, the validity of this approach is contingent upon the ability of the material to release tritium rapidly to a flush gas, such as helium. The study of tritium release rates from irradiated samples of two lithium alloys, lithium-aluminum (Li-Al) and lithium-sintered aluminum product (SAP), was completed during this reporting period. This investigation differed from current studies of solid aluminum blanket materials at other laboratories because of the low (ppm) lithium content, the incorporation of oxygen (18 wt % Al_2O_3) within the samples (i.e., SAP), and the use of large (~2.5-cm-long wafers) samples with known dimensions rather than powders.

3.3.1 Experimental procedure

The apparatus and experimental procedure used to examine tritium release rates from the aluminum alloy samples have been described previously.⁸ Basically, an irradiated sample is heated to a desired

temperature. Tritium was produced in the samples by irradiating the lithium-doped alloys at 55°C in a thermal neutron flux to achieve the desired burnup. Argon flushes the released tritium to a tritium monitor. The gas then flows through a water bubbler to remove tritiated water from the gas. Next, the elemental tritium gas from the first bubbler is oxidized in a CuO bed (600°C), cooled, and passed through another bubbler. Finally, the stream is routed through a molecular sieve trap and then to the "hot" (radioactive) off-gas stack. The rate of tritium release to the off-gas is monitored. Following the run, the sample is removed and dissolved to measure the residual tritium content.

3.3.2 Results and discussion

A series of eight runs was made to measure tritium release rates from irradiated SAP samples. Only one sample of Li-Al was available for experimentation. The data for all the runs are tabulated in Table 3.6. The objective of the initial run (sample 7) was to determine the lowest temperature at which a significant tritium release rate was observed; the results indicated that this occurred at about 250°C. In subsequent runs, the sample was held at the desired temperature for an average of 30 hr, with the exception of sample 5, which was heated for 121 hr. The temperatures used in the study ranged from about 350 to 500°C.

Due to the relatively long length of each run, some tritium diffused from the apparatus. Therefore, material balances of the tritium captured in the water bubblers and molecular sieve bed did not compare exactly with the monitored tritium release rate. To improve the capture of tritium, the size of the CuO bed was increased and several types of CuO were used. Apparently, the trapping efficiency was limited by HTO sorption in the

Table 3.6. Tritium release from solid blanket materials and amount captured in trapping system

	Li-SAP sample number								Li-Al sample number
	1	2	3	4	5	6	7	13	11
Temperature of sample, °C	34C-420	450	400	475	450	500	26-450	425	450
Weight of sample, g	0.4870	0.1312	0.1690	0.1440	0.2550	0.1928	0.3425	1.0480	0.8695
Sample thickness, cm	0.1143	0.0508	0.0609	0.0584	0.0609	0.0533	0.0813	0.5689	0.3124
Sample surface area, cm ²	4.5273	2.7406	3.0012	3.4681	3.7100	3.3520	3.8971	2.8942	4.5182
Length of run, hr	30	30	26.5	25	121	47	32	29	22
Tritium released from sample, mCi	3.042	4.704	0.626	2.236	2.193	17.88	4.581	1.337	91.79
Percent tritium from:									
(a) First water bubbler	11.9	4.3	12.2	3.8	0.9	1.1	11.7	2.9	1.5
(b) Second water bubbler	32.8	76.5	52.2	83.9	53.3	23.6	4.0	79.9	42.3
(c) Molecular sieve bed	8.5	?	?	9.8	8.4	3.3	3.1	6.5	1.9
(d) Exhaust monitor	10.3	0.3	1.7	0.4	13.1	28.3	25.8	5.4	0.1
Percent tritium trapped	53.3	80.8	64.4	97.5	62.6	28.0	18.8	89.3	45.7
Tritium from sample dissolution, mCi	35.24	11.43	3.358	9.142	5.639	10.94	39.13	71.93	0.326
Percent tritium released	7.95	29.2	15.7	19.7	28.0	62.0	10.5	1.8	99.7
CuO weight, g, and type	29.2 Harshaw pellets	15.4 Engelhard pellets	12.4 Engelhard pellets	246.3 Fisher wire	~15 Engelhard pellets	272.2 Fisher wire	~25 Harshaw pellets	248.7 Fisher wire	248.2 Fisher wire
Total amount of tritium in sample, ppm	7.86	12.3	2.36	7.90	3.07	14.9	12.8	6.99	10.6

bubblers rather than by oxidation in the CuO beds. Also, some loss may have resulted from evaporation from the bubblers.

The percent tritium released from each sample and the total tritium concentration (ppm) determined for each sample is shown in Table 3.6. Nearly all the tritium (99.7%) in the Li-Al sample was released during the 22-hr run at 450°C. The tritium release from the SAP varied from 1.8 to 62.0%, depending on temperature, sample thickness, and the run time. The total concentration of tritium ranged from about 2 to 15 ppm.

The observed release rates follow the pattern expected for bulk diffusion of tritium in the solid. Figure 3.19 compares the tritium release rate data obtained for three of the SAP samples and the Li-Al sample. Diffusion-controlled release is indicated by the slope of one-half in these curves.

3.3.3 Improved mathematical model

Previously, diffusion coefficients were calculated by a graphical technique, using the slope of a curve of the fraction of tritium released vs the square root of the time per square of the sample thickness.¹ An improved method for determination of diffusion coefficients has been developed. The solution for transient diffusion in a plane sheet, assuming a uniform initial concentration distribution and equal surface concentrations, is as follows:⁹

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{\pi^2 (2n+1)^2} \exp \left[\frac{-Dt\pi^2 (2n+1)^2}{l^2} \right], \quad (1)$$

where

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Fig. 3.19. Tritium release from Li-Al and Li-SAP samples.

$\frac{M_t}{M_\infty}$ = fraction of substance that has diffused from the sheet at
time t ,

D = diffusion coefficient (cm^2/sec),

l = thickness of the sheet (cm),

t = time (sec).

However, this model assumes that the sample is instantaneously brought to temperature. During experimentation, the heatup time of the sample to the desired temperature was usually about 1 hr and was several hours in a few cases. Since the temperature dependence of the diffusion coefficient was not known, the solution of the combined nonsteady-state mass and heat transfer problem was not practical, and Eq. (1) was modified. The concentration profile of the sample at time t was assumed to be similar to the concentration profile that would have existed at some hypothetical time, t^* , if the sample had been instantaneously heated to temperature. Therefore, to calculate the fraction of material diffused, Eq. (1) would use $t^* + t$ in place of t . The data points were fitted to Eq. (1) by a nonlinear regression using a direct optimization program¹⁰ suggested by R. E. Barker. Thus, values for t^* and D were determined at the known temperature.

Testing of the model. To illustrate this method, a hypothetical trial case will be described. The trial material is assumed to have a diffusion coefficient with the following dependence on temperature:

$$D = 1 \times 10^{-4} \exp\left(\frac{-4922}{T}\right), \quad (2)$$

where T is the sample temperature (K). The temperature in the sample during the trial run had a dependence on time as follows:

$$T = 299 + 424 \left[1 - \exp\left(\frac{-t'}{0.944}\right) \right], \quad (3)$$

where t' is time (hr). By substituting Eq. (3) into Eq. (2), D depends only on the time during which diffusion has been taking place; that is,

$$D = f(t') . \quad (4)$$

By introducing a new time-scale Z such that

$$dZ = d[f(t')t'] , \quad (5)$$

the solution for transient diffusion in a plane sheet for a constant diffusion coefficient was made by substituting Z for Dt in Eq. (1). The new time-scale Z was determined by numerical integration in this example.

Figure 3.20 shows the temperature profile and the fraction of material released, M_t/M_∞ , during a 25-hr run.

For this hypothetical test case and for the actual experimental data, the points used to calculate D and t^* were taken after the sample was at temperature for 1 hr. For the trial case, 36 points were used starting at time equal to 7.5 hr. The mathematical model searched and determined that the best values for D and t^* were $1.1051147 \times 10^{-7} \text{ cm}^2/\text{sec}$ and 5.035 hr, respectively. This is in almost exact agreement with the expected value of D at 450°C from Eq. (2), $1.10518 \times 10^{-7} \text{ cm}^2/\text{sec}$. Figure 3.20 also shows the excellent agreement of the instantaneous release rate calculated by the model (assuming constant temperature) with the test case, except at very short times.

Use of the model. Using the described technique, diffusion coefficients could be determined for each run for the period of time while the temperature was constant, regardless of the heatup time. Table 3.7 shows

Fig. 3.20. Comparison of the fraction of material released for actual and instantaneous heatup of a hypothetical run.

Table 3.7. Diffusion coefficients of Li-SAP and Li-Al

	Li-SAP sample number							Li-Al sample number	
	1	2	3	4	5	6	7	13	11
Temperature of sample, °C	420	450	400	475	450	500	383	425	450
Sample thickness, cm	0.1143	0.0508	0.0609	0.0584	0.0609	0.0533	0.0815	0.5689	0.3124
Number of data points	28	50	47	40	187	78	21	45	36
Diffusion coefficient (D), cm ² /sec	1.398 x 10 ⁻¹⁰	4.608 x 10 ⁻¹⁰	2.204 x 10 ⁻¹⁰	2.851 x 10 ⁻¹⁰	1.324 x 10 ⁻¹⁰	1.370 x 10 ⁻⁹	6.325 x 10 ⁻¹¹	1.195 x 10 ⁻¹⁰	1.462 x 10 ⁻⁶
Time (t*), hr	9.512	3.902	0.970	1.871	3.004	6.384	9.891	26.38	0.712

the D and t^* determined for each run. Sample 13 required a slightly different treatment. The shape of this sample was cylindrical rather than like a slab. Therefore, the solution for transient diffusion in a cylinder was used, instead of Eq. (1), which is:¹¹

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{a^2 \alpha_n^2} \exp(-D \alpha_n^2 t), \quad (6)$$

where a is the radius of the cylinder (cm) and α_n are the roots of $J_0(a \alpha_n) = 0$, where $J_0(x)$ is the Bessel function of the first kind of order zero. Figure 3.21 compares the calculated and actual values of M_t/M_∞ as a function of time for samples 6, 11, and 13.

The resulting values of D are plotted in Arrhenius form in Fig. 3.22; the dependence of the diffusion coefficient on temperature for Li-SAP was found to be

$$D = 2.275 \times 10^{-4} \exp\left(\frac{-19,460}{RT}\right), \quad (7)$$

where R is the gas constant (1.987 cal/K·g-mole). The coefficient of determination for this curve is 0.6353. The diffusion activation energy of 19.46 kcal/mole for tritium in SAP is within the range of activation energies reported for hydrogen in aluminum, that is, between 9.7 and 33.5 kcal/mole.¹² The experiments with the SAP and Li-Al samples indicate that acceptable tritium removal rates are possible with blankets of these materials. Comparison of the diffusion coefficients of SAP and Li-Al (at 450°C) of 2.988×10^{-10} cm²/sec [from Eq. (7)] and 1.462×10^{-6} cm²/sec, respectively, shows that Li-Al is preferable to SAP when considering tritium release rates. By continuous extraction of tritium

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Fig. 3.21. Comparison of actual and calculated values of the fraction of tritium released from solid blanket materials.

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Fig. 3.22. Diffusion coefficients for solid Li-SAP alloy.

from SAP or Li-Al, low tritium inventories should be attainable. Therefore, the residual tritium inventory in a fusion reactor would not prohibit use of solid SAP or Li-Al material.

3.4 TNS Support Studies

J. S. Watson

During FY 1977 the Chemical Technology Division provided technical support to the Fusion Energy Division's preliminary design of a Tokamak experiment known as TNS (The Next Step). This device is intended to be the next major experiment following the Tokamak Fusion Test Reactor, which is being constructed at Princeton. This will be an ignition device and will incorporate many aspects of fusion reactors not included in any present system. One new aspect is an onsite fuel recycle system. Westinghouse Corporation was the major subcontractor for all engineering aspects of the design, including the fuel recycle system. The Chemical Technology Division followed and supervised the Westinghouse design of the fuel recycle facility. The preliminary design was completed¹³ at the close of FY 1977, and the TNS program was then reduced considerably in FY 1978 to more detailed study of a few aspects of the system; thus, further work on the fuel system is planned immediately.

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4. RESOURCE RECOVERY

The Resource Recovery Program is a new effort concerned with recovery of valuable minerals from energy-related waste streams and recovery of minerals of importance to energy production from new or secondary ores. Current efforts are limited to a single problem — recovery of metals from fly ash produced by coal combustion. Other resource recovery problems and opportunities will be investigated as time and funds permit. The program is supported by the DOE/Office of Basic Energy Sciences.

4.1 Recovery of Resource Materials from Coal Combustion Wastes

V. A. DeCarlo and R. M. Canon

4.1.1 Introduction

The total ash collected in the United States in 1975, 60×10^6 tons, consisted of 42.3×10^6 tons of fly ash, 13.1×10^6 tons of bottom ash, and 4.6×10^6 tons of boiler slag (see Fig. 4.1). The percent utilization of fly ash, bottom ash, and boiler slag is 10.6, 26.7, and 40.0, respectively. It is obvious from these statistics that fly ash presents the greatest disposal problem. As shown in Table 4.1, only six other minerals are produced in larger quantities than coal ash. This quantity of ash presents a significant waste disposal problem but, if processed, could become a source of valuable minerals. Recovery of resource materials from this waste would also decrease the volume of ash requiring disposal. Furthermore, the dependence of our nation on imported alumina, a problem of both strategic and economic importance, would be reduced. The objectives of the work reported here were to study and evaluate

Fig. 4.1. Coal consumption and ash production by U.S. electric utilities.

Table 4.1. Production of minerals and solid mineral fuels in the United States^a

Mineral	Millions of short tons		
	1972	1973	1974
Stone	920.4	1060.1	1043.5
Sand/gravel	914.3	983.6	978.7
Coal (all types)	602.4	598.5	610.0
Iron ore	77.8	90.6	84.9
Portland cement	77.9	82.7	75.9
Clays	59.4	64.3	60.7
Coal ash	46.3	49.3	59.5
Salt	45.0	43.9	46.5
Phosphate rock	40.8	42.1	45.6
Slag (air-cooled)	25.0	28.8	29.8
Lime	20.2	21.0	21.6
Gypsum	12.3	13.5	11.9

^aData taken from Minerals Yearbook, Vol. 1, "Metals, Minerals, and Fuels," U.S. Department of the Interior, 1974.

existing techniques and to develop proposed and new techniques for processing the ash. The experimental program includes studying possible processing techniques followed by development and testing of critical process steps in candidate processes on a laboratory scale for aid in identifying the optimum process flowsheet and for providing the necessary design data for a cost estimate of the process.

The basic difficulties associated with processing fly ash for mineral recovery arise from the very high temperatures (e.g., 1750°C) to which the ash has been fired and the complex structure of the residue (i.e., interlocking molecular bonds with silicon). Breaking these interlocking bonds is the key to recovery of the minerals. Electron microscope photographs of fly ash, which can best be described as powdered glass beads, are shown in Figs. 4.2-4.5.

A second circumstance prompting the development of ash utilization technology is the general desire to reduce environmental pollution through the increased utilization and recycle of waste materials generated by present industrial activities. This would require a limited treatment of the ash which could be extended to recover other resource materials, depending on the evaluation of economic and technical factors. This is also a potent force which tends to prevent the exploitation of new sources of low-grade ores for the production of these minerals.

The program is considered to have four parts, or phases, which will ultimately require the cooperation and interaction of the Oak Ridge National Laboratory, the Tennessee Valley Authority, and an industrial participant.

Fig. 4.2. Fly-ash particles, 1000X magnification.

Fig. 4.3. Cenosphere in fly ash, 1000X magnification.

Fig. 4.4. Irregularly shaped fly-ash particles, 300X magnification.

Fig. 4.5. Porous fly-ash particle, 300X magnification.

Phase I. A survey of the literature, based on existing bibliographies and other pertinent sources, was made in order to identify proposed processes for the recovery of various materials from coal utilization residues. An evaluation of the relative extent of technical development required for each process was made based on the quantity of available laboratory data and the existence of pilot-plant operation experience. From these results, we determined what specific information was required to aid in the development of various processes to produce resource materials. As an example, the presence of silica and iron in the fly ash introduces different processing problems, depending on whether acid or alkaline methods are employed. In the acid methods, much of the iron dissolves while most of the silica remains insoluble. Thus the acid processes must include procedures for removing the iron or converting it to an insoluble form. The alkaline processes must deal similarly with the silica. One real advantage of the alkaline processes is that mild steel can be used, whereas acid-resistant equipment is required for the acid systems.

Phase II. We are currently engaged in this phase of the program. Our tasks are to identify the processes that appear promising and apply physical techniques to develop these processes on a laboratory scale. Experimental work has been conducted to define variables and to determine the effectiveness of various separation techniques such as solvent extraction and magnetic and gravitational methods. These fundamental studies will form the basis for further development of continuous processing techniques. An attempt was made during this phase to select, for cost evaluation, candidate processes that appeared to be most feasible from

both a technical and an economic point of view. The experimental program attempted to develop these processes for optimizing process flowsheets and providing the necessary design data for process scale-up. Three processes were selected: lime-soda sinter, salt-soda sinter-nitric acid leach, and nitric acid leach. A preliminary cost estimate was prepared for each.

Phase III. If programmatic support is forthcoming, the results of Phase II will be used as a basis for additional work and will be utilized by a more applied minerals recovery process development program. It is hoped that this will generate the necessary data for a detailed engineering design of a bench-scale experiment.

Phase IV. Based on operating data obtained from laboratory bench-scale experiments, a demonstration plant would be designed and proposed for construction near one of TVA's power-generation facilities. Production-scale process plants should be located near large coal-burning plants to provide a concentration of source $\sim 1 \times 10^6$ tons of waste residue per year. It is anticipated that ORNL would provide part of the overall project management and would perform the necessary laboratory support work as the project development continued in this phase of the program. TVA would provide a suitable site and process feed material, while the primary project management function would be fulfilled by TVA and an industrial participant.

This work is a joint effort between the Advanced Technology Section and the Chemical Development Section of the Chemical Technology Division. Only the Advanced Technology work is reported here. During this period, a salt-soda-sinter and acid leach process was evaluated. Also, extraction methods to recover the various minerals are being developed.

4.1.2 Processes examined

Lime-sinter process. The lime-sinter process removes alumina from a refractory aluminosilicate compound with a reagent (i.e., calcium oxide from limestone) which has a stronger affinity for silica than does alumina. This is a modification of a process patented by Pedersen^{1,2} for smelting bauxite, limestone, iron ore, and coke to produce iron and calcium aluminate slag. A variation of the process was patented by Seailles and Dyckerhoff³ for sintering a mixture of limestone and high-silica alumina compound to form calcium aluminate.

Investigators^{4,5} have found that the calcium oxide:silica weight ratio should be 2 with sufficient calcium oxide to give a $\text{CaO}:\text{Al}_2\text{O}_3$ weight ratio of 5:3 in order to release alumina from silicated compounds.

The lime-sinter process has been the subject of considerable research by Murtha et al.,⁶ as well as by Grim, Machin, and Bradley.⁷ Some of the work done on clays indicated an optimum sintering temperature range of 1370 to 1390°C.

The process development reported here first attempted to duplicate experiments reported in the literature; then parameters were varied in an attempt to increase the yield of alumina. Unfortunately, we were unable to achieve our objective. Figure 4.6 shows the sequence of operations of the process. A cost estimate of this process was not made because of the greater yield of alumina from the lime-soda-sinter process.

(Equipment and procedure). The fly ash used in these tests was obtained from the TVA Kingston Steam Plant; its analysis is given in Table 4.2. Although the material was received dry, it was slurried with water to represent the form of ash that is being suggested as the process feed.

Fig. 4.6. Lime-sinter process.

Table 4.2. Analysis of fly ash from TVA Kingston Steam Plant

Constituent	wt %	Constituent	wt %	Constituent	ppm
SiO ₂	49.4	Si	23.1	Ba	38
Al ₂ O ₃	27.96	Al	14.8	Cr	129
Fe ₂ O ₃	10.77	Fe	7.53	Cu	194
MnO ₂	0.30	Mn	0.19	Ni	221
CaO	1.51	Ca	1.08	Rb	245
MgO	1.38	Mg	0.83	S	1800
TiO ₂	1.68	Ti	1.01	Sr	880
K ₂ O	3.14	K	2.61	V	180
				Zn	233

(Magnetic separation). Some existing processes use a preliminary magnetic iron separation step in an effort to mitigate the problem of removing iron from the alumina and to provide a lower iron level in cement. We used various techniques to determine an effective means for removing magnetic iron from fly ash. The most suitable method, with the available equipment, appeared to be a wet separation followed by drying of the two fractions. The fly ash was slurried with water and placed in a separatory funnel surrounded by permanent magnets outside the glass surface. The more-magnetic-particles, which contained a higher percentage of iron, were retained on the inside surface of the glass. The ash was recycled six times. Approximately 10 kg of the fly ash has been processed in this manner to provide a fly-ash fraction low in magnetic iron for those studies in which a low-iron fraction appeared to be an advantage. Upgrading of the magnetic fraction would provide a salable product. The following table summarizes typical data obtained by use of this method for removing magnetic iron from fly ash:

	<u>Before magnetic separation</u>	<u>After magnetic separation</u>	
		<u>Magnetic fraction</u>	<u>Nonmagnetic fraction</u>
Weight, g	100	12	86
Fe, g	7.21 (100%)	3.74 (52%)	3.50 (48%)
K, g	2.54 (100%)	0.17 (7%)	2.2 (87%)

Although 52% of the total iron was removed by this procedure, the iron-rich fraction is not a salable product because blast furnace feed specifications require 60% iron content and <0.15% potassium. Because the magnetic separation step is simple and the less-magnetic fraction of the

fly ash is more suitable for cement manufacture, it is apparent that additional research is warranted. More efficient iron recovery is possible,⁶ but the problem of potassium separation has not been resolved. The economics would need to be evaluated after the cost of upgrading the iron oxide has been calculated to determine whether the process should be included in a final flowsheet.

(Sintering). The wet, nonmagnetic fly-ash fraction was partially dried and mixed with a calculated quantity of CaCO_3 to give $\text{CaO}:\text{Al}_2\text{O}_3$ and $\text{CaO}:\text{SiO}_2$ mole ratios of 1.79 and ~ 2.0 respectively.⁸ Mixing took place during wet grinding of the material to -100 mesh. After four attempts, a mixture was prepared which self-disintegrated when cooled after sintering at 1380°C for 1-1/2 hr. Self-disintegration of the sinter is considered desirable to eliminate the necessity of additional grinding. Rapid cooldown of the sintered mix apparently aided self-disintegration. The furnace allowed the sample to be heated to 1380°C in 2 hr and cooled so that it could be removed in 2 hr at 200°C .

The chemical reactions that occur are

The sintering temperature was not varied because the literature⁶ indicated that sintering at 1380°C allowed the largest percentage of soluble alumina to be recovered. The reaction time was varied between 1 and 3 hr in an effort to promote self-disintegration, which occurred at a reaction time of 1-1/2 hr; however, more research is needed to optimize this step.

(Leaching). The weight loss during sintering is ~30%, due primarily to loss of moisture and CO_2 . The sintered ash was leached for 15 min at 65°C with a 3% solution of Na_2CO_3 to provide 1.66 moles of Na_2CO_3 for each mole of Al_2O_3 present in the material.⁷ (The Na_2CO_3 solution can be recycled from a soda ash recovery section.) To maintain the proper concentrations of soda, alumina, and carbonate in the pregnant liquor, CO_2 gas was added to the solution during leaching. The mixture was filtered, and the filtrate was washed free of soluble soda, alumina, and carbonate. The chemical reactions that occur are believed to be

Reaction (5) is the most desirable; however, the other two reactions also occur. Based on analyses of the filtrate and the residue of one run, the best yield of alumina extracted was 56.6 and 67.2, respectively. Further research is needed to optimize the leaching conditions to increase the yield of alumina.

(Cement). The tailings of the Na_2CO_3 leaching were sintered at 1094°C for 2 hr, which removed all the water and CO_2 . The sintering temperature and reaction time are the same as those used for the production of portland cement. The material from this second sinter formed clinkers. A quantity of gypsum not to exceed 3 wt % of the resulting cement (which is the maximum quantity allowed) was added as CaSO_4 and subsequently mixed and ground.

Water was then added to the cement to make concrete. The resulting product seemed reasonably strong but was not subjected to any quantitative tests. The determination of optimum conditions to produce the best quality of cement was not included in this study because of time limitations; however, this would be a very important part of any further research.

(Desilication). Desilication of the pregnant solution from the Na_2CO_3 leaching step is necessary because of the high concentration of silica in the solution. The lime for this step was obtained by calcining limestone at 1200°C . The lime was slurried with 10% of the pregnant liquor before it was added to the desilication step. The filtrate from the leaching step was mixed with calcined limestone. Calculations indicated that 0.5 wt % limestone would be required to desilicate the solution. The mixture was heated in an autoclave for 2 hr at 175°C and 200 psi. The conditions given for this step in the literature⁹ are a temperature of 175°C and a pressure of 100 psi. We decided to use a higher pressure in an attempt to increase the yield; however, our efforts were unsuccessful. The desilicated solution was cooled, filtered, and washed. The chemical reaction that occurs is as follows:

More research will be required in order to optimize the temperature and pressure for the reaction.

(Carbonation). The desilicated solution was carbonated at 75°C for 24 hr by passing CO_2 through the solution. (The CO_2 gas used in this operation could be obtained from the sintering step.) Fine alumina trihydrate crystals were added as seed to aid in precipitation; an

equivalent of 25 wt % of the alumina that precipitates is required.⁸ The filtrate was then washed and dried. The chemical reaction that occurs is

This step is straightforward; the time at temperature could probably be reduced.

(Calcination). The alumina trihydrate from the carbonation section was calcined at 1100°C for 2 hr to form alumina. The chemical reaction that occurs is

This step is straightforward, and no further research is required.

Lime-soda-sinter process. The first lime-soda-sinter process was developed by Adolf Kayser⁹ in 1902 to separate alumina from silica. In 1947, Conley et al.¹⁰ developed a process for separating alumina from clay. During World War II, a 50-ton/day plant was built in Wyoming to produce alumina from anorthosite; however, it was never put into operation.

In the process we investigated, the fly ash is mixed with limestone and soda ash in a wet grinding step, and the resulting mixture is sintered to convert the alumina to sodium aluminate and the silica to dicalcium silicate. The sintered product is leached with a dilute Na_2CO_3 solution to dissolve sodium aluminate from the sinter, and the resulting slurry is processed to remove the residue from the leach liquor. The pregnant solution is treated with lime in an autoclave to precipitate dissolved silica, which is then removed by settling and filtration. The desilicated liquor is carbonated to precipitate alumina trihydrate, which is

then separated from the liquor, washed, and calcined to produce alumina. The tailings from the leaching step are sintered and mixed with gypsum during grinding to form cement. An overall flowsheet of the sequence of operations is shown in Fig. 4.7.

(Sintering). The fly ash was processed wet in a magnetic separation step to remove the magnetic fraction. The nonmagnetic portion of the fly ash (~85%) was partially dried and mixed with limestone and a soda ash solution in a wet grinding step to obtain a -200-mesh material. The quantities of limestone and soda added were sufficient to produce a mixture containing 1 mole of soda per mole of alumina and 2 moles of CaO per mole of silica. This method differs from the lime-sinter process in that the Na_2CO_3 is mixed with the fly ash plus CaCO_3 prior to sintering. The literature indicates that a significantly higher recovery of Al_2O_3 can be obtained using this method.⁷ The disadvantage is that the Na_2CO_3 must be washed from the residue prior to processing it into cement.

The first lime-soda-sinter (fly ash + limestone + Na_2CO_3) experiment was carried out at 1380°C with poor results. The mixture formed a glass-like melt that did not appear suitable for further processing because of the potential difficulty of grinding. Apparently, the sintering temperature was too high in this experiment. A second lime-soda sinter, which was performed at 1250°C for 30 min, was much more successful. Although it failed to self-disintegrate to a powder, it did form a grainy, cracked solid that was very easily ground with mortar and pestle to -65 mesh. Another sinter made under the same conditions gave the same result. The reactions that occur are believed to be

Fig. 4.7. Lime-soda-sinter process.

Further research is required to optimize the sintering temperature and concentrations of limestone and sodium carbonate.

(Leaching). A sample of the sintered product was mixed with a Na_2CO_3 solution and leached for 15 min at 95°C .¹¹ Approximately 2 g of leaching solution was found to be required per gram of sintered material. The slurry produced by leaching was filtered, and the residue was washed. (Part of the wash can be recycled to the leaching solution.) Four portions of the sintered product were leached, using different Na_2CO_3 concentrations and leach times. The results are given in the following table:

<u>Leach No.</u>	<u>Na_2CO_3 conc. (M)</u>	<u>Leach time (min)</u>	<u>Percent alumina recovered^a</u>
6A1	1.11	15	58.5
6A2	0.56	15	61.1
6A3	0.56	60	43.4
6A4	2.23	15	37.4

^aIn the filtrate.

The steps following the sintering and leaching steps are similar to those of the lime-sinter process.

Acid leaching. A moderately high extraction of aluminum was achieved in three single-stage nitric acid leaches in which the pulp density was maintained at 10% solids. In these tests, either 8 N or 12 N HNO_3 was used as the leachant, and the contact time was 24 to 48 hr at reflux temperature. The feed fly ash was the magnetically separated, low-iron fraction. Leaching data for aluminum, titanium, and iron, based on analyses of both the filtrate and residue, are shown in Table 4.3.

Table 4.3. Leaching of nonmagnetic fraction of Kingston fly ash with HNO_3 under reflux conditions

Leaching conditions: temperature, $\sim 110^\circ\text{C}$; pulp density, 10% solids

HNO_3 conc. (<u>N</u>)	Time (hr)	% Al leached		% Ti leached		% Fe leached	
		Filtrate	Residue	Filtrate	Residue	Filtrate	Residue
8	24	56.9	54.6	29	30	57	50
8	48	69.7	63.4	32	37	37	33
12	48	71.3	62.0	22	38	33	41

4.1.3 Economic evaluation

Three of the processes examined in our investigations appear to have merit for processing fly ash. These are: lime-soda-sinter, salt-soda-sinter-nitric acid leach, and nitric acid leach. Schematic flowsheets of the three processes are shown in Figs. 4.7, 4.8, and 4.9. In order to make the three processes comparable, the bases of design were fixed as follows:

Fig. 4.8. Salt-soda-sinter process.

Fig. 4.9. Nitric acid leach flowsheet.

1. The plant capacity is 1×10^6 tons of fly ash (dry basis) per year as slurried product from the fossil-fueled plant collectors, containing 66 wt % water.
2. The fly ash to be processed is obtained from the TVA Kingston Steam Plant.
3. Removal of an iron-rich fraction by magnetic separation is the first step in each process.
4. The plant is located at the TVA Kingston Steam Plant site.

Summaries of the cost estimates of three of the processes investigated are given in Table 4.4. Since the flowsheets on which the cost estimates were based are conceptual, the costs should be considered preliminary. This type of estimate prepared from a flowsheet and a minimum of equipment data can be expected to be fairly inaccurate (i.e., within 30% of the actual cost). However, such estimates can be used legitimately to make a comparison of processes because the evaluation methods are identical in each case. Results of the comparison showed reasonable agreement in the costs of the plants; however, the operating costs were significantly different. The income from products for the lime-soda-sinter and salt-soda-sinter processes is high because of the large quantity of cement and silica gel produced. A market for such amounts of product would need to be found before these profits could be considered realistic. The uncertainty arises from the fact that pricing of a product depends on form, purity, suitability as input to other processes, and quantity of product to be sold. The quantities of ash consumed for the lime-soda-sinter, salt-soda-sinter-nitric acid leach, and nitric acid leach processes are 90, 60, and 30%, respectively. From

Table 4.4. Summary of cost estimates for recovery
of resource materials from fly ash

1×10^6 tons/year (dry basis)

Process	Cost of plant ^a (\$)	Annual operating cost (\$)	Income from products (\$)
Lime-soda sinter	61,892,000	43,393,055	119,542,975
Salt-soda-sinter- nitric acid leach	58,006,000	32,461,475	109,191,573
Nitric acid leach	66,316,000	22,448,150	31,114,425

^a If land and utilities are not available, add 30% to plant costs.

a total ash usage viewpoint, the lime-soda-sinter has considerable merit, provided a market can be found for the cement produced.

4.1.4 Summary

It is concluded from our studies that additional research is necessary to determine the optimum method for processing fly ash for recovery of resource materials. Evaluation of the economic and technical factors indicates no significant differences in the three processes for which cost estimates were prepared; however, a study of the marketability of the products and a detailed estimate of the costs to produce them would be necessary to show which of the processes is the most desirable. The most economical process may be one that combines disposal or environmental credits with product values to help "pay its way."

4.1.5 Future work

From the data obtained to date, we have identified the following areas of research which require additional development. These steps in the various processes will first need to be ordered according to the importance of their economic and technical aspects.

1. Process step to remove cenospheres, which are fly-ash particles that float; such material is useful¹² and has a potential value of \$100/ton. The quantity in the TVA Kingston fly ash is ~1 wt %.
2. Equipment to provide optimum removal and concentration of magnetic iron and development of a separation technique that reduces the quantity of potassium in the magnetic iron fraction from the fly ash. If development efforts

are unsuccessful, the total iron may be removed as high-grade iron in certain processes by special separation techniques.

3. Lime-soda-sinter process

- (a) Sintering — $\text{CaO}/\text{Al}_2\text{O}_3$ and CaO/SiO_2 mole ratios, along with sintering temperature, reaction time, and rate of cooldown need to be optimized.
- (b) Leaching — $\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3$ mole ratio needs to be optimized.
- (c) Desilication — temperature and pressure in this reaction need to be optimized.
- (d) Products of the lime soda sinter process, which go into cement, need to be varied and a study made of the materials that can be added to yield the type of cement in demand.

4. Economic analysis of product value vs purity from the various treatment processes being considered to determine realistic costs due to losses of solvents and acids for the various processes.

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