Title

OXYDESULFURIZATION OF COAL BY ACIDIC IRON SULFATE SOLUTIONS

Author

Mixon, D.A.

Publication Date

1981-08-01

Thesis/dissertation

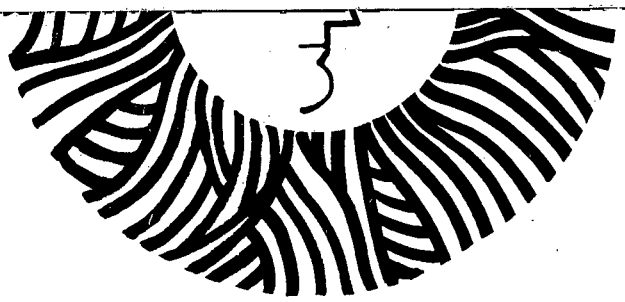
Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT
DIVISION

OXYDESULFURIZATION OF COAL BY ACIDIC IRON SULFATE SOLUTIONS

David A. Mixon and Theodore Vermeulen

October 1979



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

DISCLAIMER

OXYDESULFURIZATION OF COAL BY ACIDIC IRON SULFATE SOLUTIONS

David A. Mixon and Theodore Vermeulen

ABSTRACT

To facilitate byproduct recovery and eliminate elemental sulfur formation, a high-sulfur bituminous coal (Illinois No. 6) has been treated with aqueous ferric sulfate/sulfuric acid and oxygen at 100-150°C for pyrite removal. Conversions up to 56% in 1 hour have been obtained with -20/+35 mesh coal at 280 psi of oxygen. Relatively complete pyrite removal by this method appears feasible; also, the possibility exists of extending the method to remove at least part of the organic sulfur present.

OXYDESULFURIZATION OF COAL BY ACIDIC IRON SULFATE SOLUTIONS

David Mixon and Theodore Vermeulen

An extensive exploratory set of coal desulfurization experiments has been run, using aqueous solutions of H_2SO_4 and $Fe_2(SO_4)_3$ to oxidize pyrite. The motivation for using H_2SO_4 has been twofold-- to create conditions that would avoid formation of elemental sulfur (since S^0 is considered to be unstable in an oxidizing environment), and to facilitate the recovery of H_2SO_4 and $Fe_2(SO_4)_3$ as saleable products. This latter purpose is aided by the insolubility of $Fe_2(SO_4)_3$ at high weight ratios of H_2SO_4 to water. To monitor the presence of elemental sulfur, we have developed a new UV-spectrophotometric method applicable to both untreated and treated coal.

The coal used in our runs is an Illinois No. 6 bituminous, with the chemical distribution of sulfur content shown in Table 1. Since it is desirable to minimize coal-grinding costs in large-scale operations, a medium grind (-20 +35 mesh) has been used; runs on more finely ground coal are now scheduled. Most other desulfurization studies have utilized coal particle sizes below 100 mesh.

A previous study by Meyers[1] of aqueous oxidation with a solution containing 5 wt-% iron, without recycle of product H_2SO_4, run at 120°C with 100 psi of oxygen for 90 minutes, has demonstrated 85% removal of pyritic sulfur. Meyers reports the composite stoichiometry:

$$FeS_2 + 2.4\ O_2 \longrightarrow 0.2\ Fe_2(SO_4)_3 + 0.6\ FeSO_4 + 0.8\ S$$

The elemental sulfur so formed must be removed in an additional processing step, either vaporizing or solvent-extracting it.

To guide the selection of conditions for coal treating and byproduct recovery, Figure 1 has been developed to correlate the $Fe_2(SO_4)_3$ solubility

Table 1. Analysis of Untreated Illinois No. 6 Coal, MAF[1], wt-%

Sample no.	1	2
Mesh size (Tyler screen no.)	-20 +35	-20 +35
Total sulfur [2]	4.77	4.32
Pyrite sulfur	1.13	1.18
Sulfate sulfur	0.97	0.44
Elemental sulfur	-[3]	0.09
Organic sulfur, by difference	2.67	2.62
Sulfur-free mineral matter ("ash")[4]	13.17	18.06
Runs made		
Atmospheric	2-5	6-8
Pressure	1-8	9-10

Footnotes

[1] Moisture- and ash-free

[2] Eschka method

[3] Undetermined

[4] Corrected from Fe_2O_3 to Fe (without sulfur)

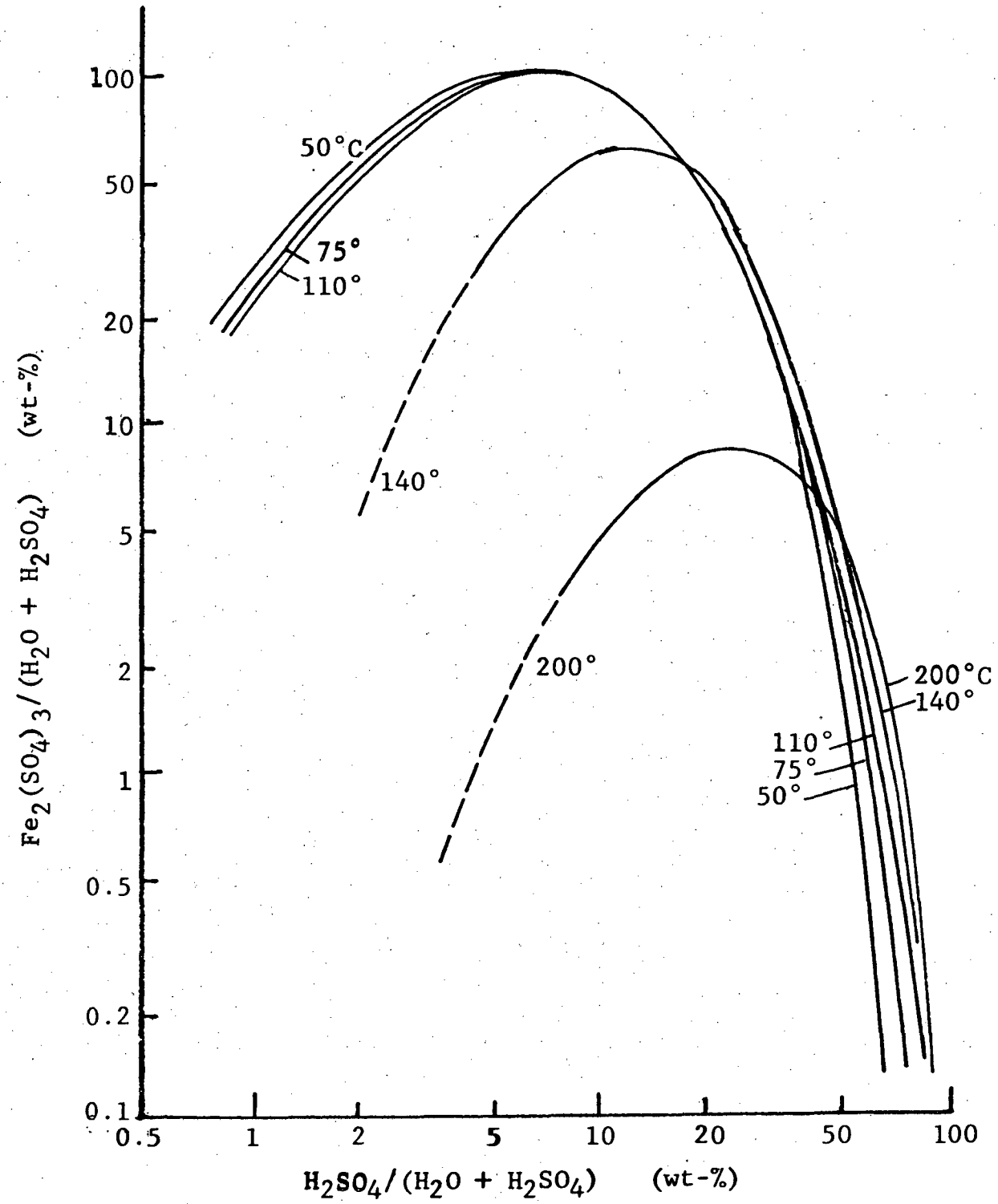


Figure 1. Solubility of $Fe_2(SO_4)_3$ in Aqueous Sulfuric Acid.
(After Posnjak and Merwin, ref. 2.)

as a weight ratio to total H_2SO_4 plus H_2O, as a function of the ratio of H_2SO_4 to total H_2SO_4 plus H_2O[(2)].

Atmospheric-Pressure Runs

Atmospheric runs were performed in a four-neck round-bottom glass flask equipped with a sparger of 304SS or of glass. Runs A2 - A5 were made to investigate the effect of H_2SO_4 concentration in solutions of $Fe_2(SO_4)_3$ at about 80% of its solubility limit. Table 2 shows the run conditions, and the results obtained. The best pyrite removal, about 40%, occurred with 15% H_2SO_4, in run A3. However, about one-fourth of the pyrite reacted appeared to form elemental sulfur which remained in the coal. In run A4, with 5% H_2SO_4, the apparent formation of elemental sulfur was much lower.

Analysis for Elemental Sulfur

The need for direct knowledge of elemental sulfur content led us to develop a direct method for its analysis. Elemental sulfur is known to exhibit UV absorbance around 220nm. We measured its absorbance and solubility in a number of UV-transparent organic solvents. A procedure was adopted involving cyclohexane extraction of coal for an extended period, and subsequent spectrophotometric analysis of the extract. Interfering absorbance by extractible organic compounds in the coal was overcome by first measuring the combined absorbance, then removing the elemental sulfur by reaction with acid-cleaned copper strips, then remeasuring the absorbance and taking the difference at two wavelengths, 265 and 280 nm. The respective extinction coefficients are 56.5 and 53.5 $(cm \cdot gm/liter)^{-1}$, as shown in Figure 2.

In run A8, similar to run A3, direct analysis of elemental sulfur showed that 17% of the pyrite sulfur converted formed elemental sulfur.

Table 2. Atmospheric-Pressure Runs (100°C, 1 hr.); Analyses on MAF Basis

Run no.	A2	A3	A4	A5	A6	A7	A8
Coal sample used	1	1	1	1	2	2	2
Coal loading, gm	40	40	40	40	20	20	20
Solution loading, gm	160	160	160	160	110	110	110
$H_2SO_4/(H_2O + H_2SO_4)$, wt-%	25	15	5	15	35	40	15
$Fe_2(SO_4)_3/(H_2O + H_2SO_4)$, wt-%	24	48	76	48	0	0	48
Solution density at 25°C, gm/ml	1.36	1.44	1.50	1.44	1.27	1.30	1.44
O_2 flow, l./min	0.5	0.5	0.5	0.5	0.3	0	0.3
Added reactants	none	none	none	NaCl[1]	V_2O_5[2]	H_2O_2[3]	none
Relative stirring speed, rpm.	125	125	125	125	300	300	300
Sulfur removed, %							
Total	12.5	13.5	10.4	9.1	added	22.7	1.0
Pyrite	26.1	39.8	31.2	6.3	2.2	86.9[4]	26.8
Sulfate	36.4	35.9	15.7	36.5	added	added	added
Elemental	0[5]	0[5]	-[6]	-[6]	-[6]	57.0	-63.7
Organic [5,6]							
Sulfur-free mineral removed, %	27.4	24.6	20.3	15.9	16.3	undet'd	12.9
(Fe^{+++}/total Fe) in final soln., %							88.8

Footnotes: See next page

Footnotes

(1) 5% NaCl (relative to H_2O + H_2SO_4); highly corrosive

(2) Added as 1.00 gm NH_4VO_3

(3) The 40% H_2SO_4 medium included 3mM $NiSO_4$ as catalyst. Starting at 40°C, we added 10 wt-% relative to H_2O + H_2SO_4) of 30% H_2O_2 dropwise over 40 min., with slow stirring, the heat of reaction bringing temperature to 80°C in 20 min. Mixture was then held at 100°C for 1 hr.

(4) Based on total-sulfur percentage

(5) Inferred from a calculated increase in elemental S + organic S
(= total S - pyrite S - sulfate S)

(6) Negligible change (explicitly in run A8, implicitly elsewhere)

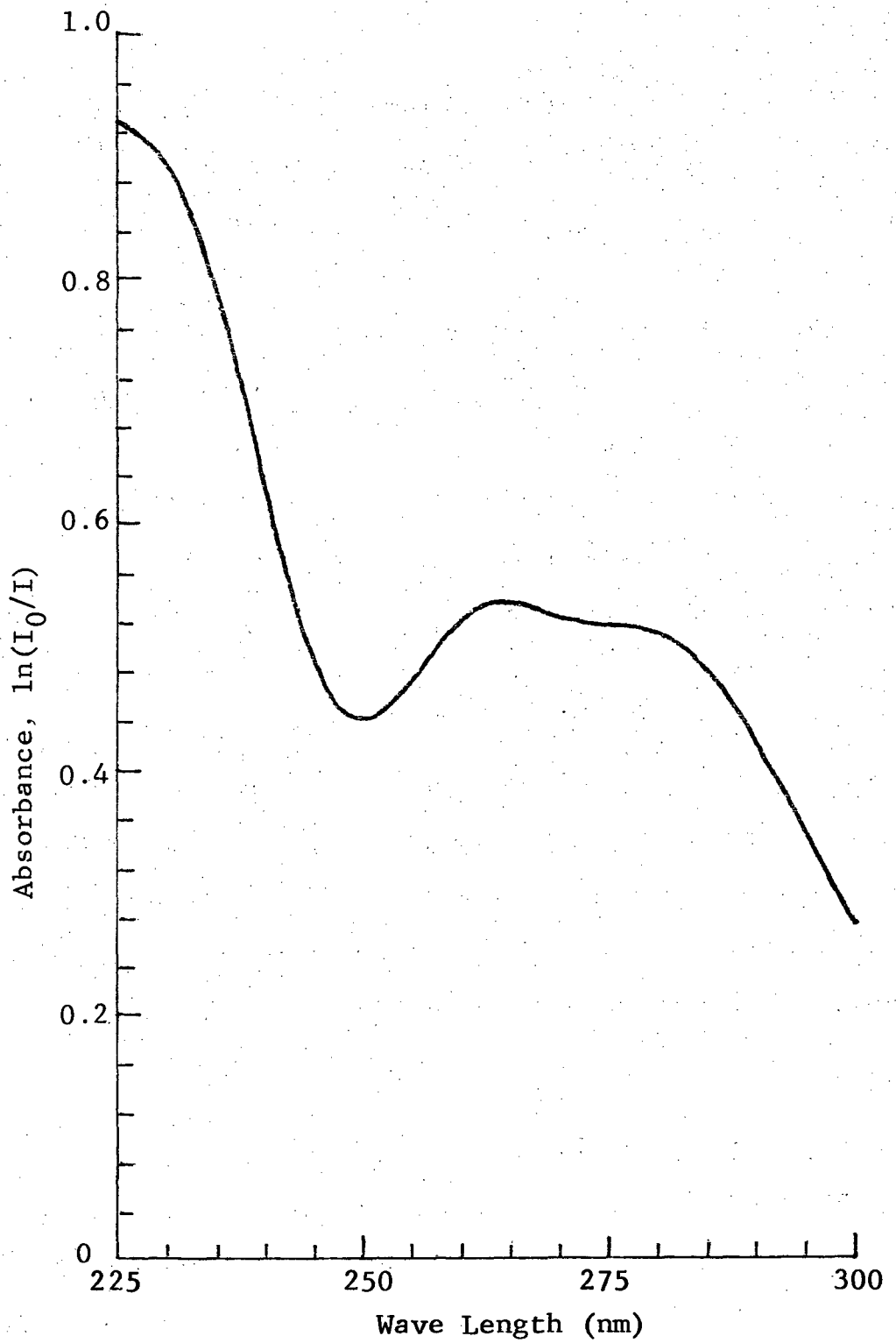


Figure 2. Ultraviolet absorbance for S^0 in cyclohexane at a concentration of 10 mg/liter, measured on a Cary 219 spectrophotometer for a band width of 1.0 nm.

This result, together with the low total conversions of pyrite, indicated that atmospheric-pressure reaction conditions (temperature 100°C, and O_2 partial pressure about 0.4 atm) are not satisfactory even for pyrite removal.

Run A6 with ferric sulfate replaced by ammonium vanadate, in 35% H_2SO_4, gave an extremely low pyrite conversion, only 2%. This run established that H_2SO_4 and oxygen, without iron, are ineffective at 100°C; also that vanadium salts cannot substitute for ferric iron in the pyrite oxidation process. The possibility that vanadium will accelerate the re-oxidation of ferrous to ferric iron remains to be studied.

Departing from the use of ferric iron or molecular oxygen as primary oxidant, hydrogen peroxide was used in an exploratory experiment (run A7) in 40% H_2SO_4, with a nickel catalyst to promote the equilibrium formation of peroxy sulfuric and species such as H_2SO_5. Reaction was rapid, as shown by vigorous heat release, and resulted in 87% conversion of pyrite. This experiment was a variation of reaction conditions described by M. Dondelewski (Columbus, Ohio), in a pending U. S. patent.

Higher-Pressure Runs

Experiments at higher temperatures and pressures were carried out in a 600-ml Parr autoclave constructed on Type 316 stainless steel and fitted with a glass liner. Table 3 shows the conditions and results for the ten runs completed so far.

For a treating solution with 15% H_2SO_4 and 48% $Fe_2(SO_4)_3$, relative to (H_2O + H_2SO_4), the results at 140-150 psi of O_2, at both 100°C and 150°C (runs P1 and P3) gave less pyrite converstion than in the comparison

Table 3. Higher-Pressure Runs (150°C, 1 hr.); Analyses on MAF Basis

Run no.	P1 [1]	P2	P3	P4	P5	P6	P7	P8	P9	P10
Coal sample used	1	1	1	1	1	1	1	1	2	2
Coal loading, gm.	40	40	20	20	20	20	20	20	20	20
Solution loading, gm.	160	160	110	110	110	110	110	110	110	110
$H_2SO_4/(H_2O + H_2SO_4)$, wt-%	15	15	15	25	15	15	25	25	25	25
$Fe_2(SO_4)_3/(H_2O + H_2SO_4)$, wt-%	48	48	48	24	48	48	12	12	12	12
Solution density, 25°C gm/ml	1.44	1.44	1.44	1.36	1.44	1.44	1.27	1.27	1.27	1.27
Partial pressure of O_2, psia	150	200	140	140	0	0	140	140	140	280
Total pressure, psia	160	275	215	215	75	75	215	215	215	355
Added reactants	-	-	-	-	-	$FeSO_4$ [2]	-	-	-	-
Stirring speed, rpm	200	200	400	400	400	400	400	525	750	750
Sulfur removed, % [2]										
Total										
Pyrite	21.5	43.5	19.5	26.3	18.6	21.3	31.9	38.1	34.4	56.3
Sulfate										
Elemental										60.7
Organic										
Sulfur-free mineral removed,%	16.8	20.5		10.4		2.3	6.4	12.5	26.2	30.6
(Fe+++/total Fe), final, %			80.6	72.9	56.0	55.5	60.4	67.5	81.4	86.5

Footnotes

(1) 100°C

(2) In this set of runs, attention was focused on pyrite content.

atmospheric-pressure runs (A3 and A8). Reduced oxygen solubility at the higher temperature, along with poorer stirring efficiency, could explain these results. Similar conversions of around 20% of the pyrite were obtained without any oxygen; and excess $FeSO_4$ was found to have no influence on the rate. For the same H_2SO_4 and $Fe_2(SO_4)_3$, 200 psi of O_2 at 150°C gave 43% conversion, suggesting that O_2 partial pressure is a major factor.

A solution of 25% H_2SO_4 and 24% $Fe_2(SO_4)_3$ at 140 psi O_2 and 150°C, in run P4, gave a more modest increase in conversion to 26%. This suggested that H_2SO_4 is a more important factor than the ferric iron. Changing to 25% H_2SO_4 and 12% $Fe_2(SO_4)_3$ gave 32% conversion in run P7 at 400 rpm, and 38% in run P8 at 525 rpm. A further increase in stirring speed to 750 rpm (run P9) with another coal sample gave a conversion of only 34%, suggesting that 525 rpm is probably sufficient for this reactor configuration.

Runs at pressures above 150 psi of O_2 showed progressively superior conversion; P2, at 200 psi with only 200 rpm stirring, gave 43%; and P10, at 280 psi with 750 rpm, gave 56%. Even higher pressures, with optimum stirring, temperature toward 200°C, and perhaps more finely ground coal, may hold the key to complete pyrite removal in a residence time of one hour or less.

Conclusions

On the basis of about 20 experimental runs, it is predicted that 90% removal of pyrite from Illinois No. 6 bituminous coal could be accomplished by using the following treating conditions:

- 150-180°C temperature
- 400 psi oxygen
- minus-40-mesh coal
- 60-minute residence time or less

. 25% H_2SO_4 and 12-15% $Fe_2(SO_4)_3$, both expressed relative to (H_2O + H_2SO_4) content

. 35-40 vol-% solids loading of the reactor

Addition of catalysts or supplementary reactants to this system may also result in substantial conversion of organic sulfur present in such coal.

References

(1) R. A. Meyers et al., Science, 177, 1187 (1972); U. S. Patent No. 3,768,988 (1973).

(2) E. Posnjak and H. E. Merwin, J. Amer. Chem. Soc., 44, 1965 (1922).

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720