DOE/PC/93226--T8

INVESTIGATION OF MINERAL TRANSFORMATIONS AND ASH DEPOSITION DURING STAGED COMBUSTION

Quarterly Technical Progress Report
April 1, 1995 to June 30, 1995

John N. Harb
Brigham Young University
Provo, Utah 84602

Date published- July 31, 1995

RECEIVED
USDOE/PETC
95 AUG -7 AM 11: 12
ACQUISITION & ASSISTANCE DIV.

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Contract No. DE-FG22-93PC93226

HH

FOREWORD

This report summarizes technical progress during the seventh quarter (April 1, 1995 to June 30, 1995) of a three-year study conducted for the Department of Energy (DOE) under Contract No. DE-FG22-93PC93226. The principal investigator for this work was Dr. John N. Harb; Mr. James Hickerson was the technical representative for DOE.

The technical work reported for this quarter was performed by graduate students Neal Adair and Peter Slater. Bret Abbott, Eyas Hmouz, and Rachel Newsom, undergraduate students in chemical engineering at BYU, also made important technical contributions to this report.

ABSTRACT

Progress during the seventh quarter of a three-year study was made in four task areas: 1) analysis of coals, 2) improvements to the reactor system, 3) parametric testing of the target coals, and 4) analysis of samples from the combustion tests. A problem with our analysis system was discovered and corrected. Recent analyses of the Pittsburgh #8 coal (after repulverizing) were redone and the results are reported. A new design of the deposit probe and an air preheater were added this quarter. Parametric testing of the Pittsburgh #8 coal continued this quarter. Analytical results from these tests show sulfur release and iron transformations as a function of test conditions and sampling location. Deposit samples were also collected from the Pittsburgh coal at three different stoichiometric ratios. Operating conditions appeared to have a significant effect on deposit formation. Finally, specific tasks for the next quarter have been identified and reported.

OBJECTIVES AND SCOPE

A. Background

A thorough understanding of the fundamental processes which govern the mineral behavior is essential to the development of tools to predict and manage ash deposition. The purpose of the current project is to perform a fundamental study of mineral transformations and ash deposition during staged combustion of pulverized coal. Staging of combustion air is a strategy used to reduce NOx emissions from coal-fired units. It is applicable to both advanced combustion systems currently under development (e.g. HITAF) and low NOx retrofits for existing units. These low NOx combustion strategies produce fuel rich or reducing conditions in the lower furnace. Therefore, the combustion history of the coal particles is significantly changed from that experienced under normal combustion conditions. A carefully designed experimental study is needed to examine the effects of altered combustion conditions on mineral matter release, fly ash formation, particle stickiness and deposit formation. This project uses state-of-the-art analytical equipment and a well-characterized laboratory combustor to address this need.

B. Objectives

This report describes work in the seventh quarter of a fundamental, three-year study of mineral transformations and ash deposition during staged combustion. The objectives of this project are:

1) Creation of an experimental database which documents the behavior of inorganic constituents during staged combustion under well-defined conditions,

2) Identification of key mineral species or reactions which may be problematic,

3) Development of increased understanding and insight into the mechanisms which control ash formation and deposition.

C. Research Task Summary

Task 1: Select specific coals, prepare the coals for use in the laboratory combustor, and perform a detailed characterization of samples from the prepared coals.

Task 2: Prepare and test reactor facilities and sampling probes for use in the proposed experiments.

Task 3: Conduct a parametric study of mineral transformations and particle stickiness during staged combustion by performing a series of tests at a variety of conditions and collecting both particulate and deposit samples for each of the tests.

Task 4: Analyze particulate samples collected in Task 3 in order to determine the size, shape, and composition of the particles. Also, examine particle stickiness by analyzing the composition (bulk and local) and morphology of deposits collected as part of Task 3.

Task 5: Design and perform additional tests based on the results of Tasks 3 and 4 in order to define mechanisms, identify critical conditions, etc.

PROGRESS REPORT

This section of the report describes progress made during the seventh quarter. Progress is summarized by task.

Task 1

Last quarter we reported that the pyrite in the Pittsburgh #8 coal appeared to be partially oxidized (weathered) based on our SEM/EDS analysis. An additional sample of coal was obtained this quarter to verify that oxidation had indeed taken place. The new coal (also Pittsburgh #8) was obtained from Consol, Inc. and stored under nitrogen prior to testing. Analysis of the coal with the SEM indicated that this coal was also oxidized, contrary to expectations given the history of the coal prior to analysis. Moreover, sulfur analysis of the new coal showed large amounts of pyritic sulfur. *Consequently, we concluded that the problem was with our analysis and not with the coal.* In other words, the coal had not oxidized to any appreciable extent and our analysis was incorrect. The source of the analysis problem turned out to be an improper calibration of the pyrite standard. The problem occurred when our new microanalysis system was quickly put into service. The system has been recalibrated and the DOE coal has been reanalyzed. In addition, the calibration has been checked independently by another research group. The new results for the DOE coal (Table 1) show significant quantities of pyrite as expected.

Table 1
Pittsburgh #8 Mineral phases from SEM/EDS analysis

Mineral	% of total
Quartz	7.06
$Fe_2O_3/FeCO_3$	.96
Aluminosilicate	31.55
Ca-Al-Silicate	1.24
Fe-Al-Silicate	2.22
K-Al-Silicate	12.79
Pyrite	10.82
Calcite/CaO	7.72
$FeS/FeSO_4$	.63
Unknown	21.18

It appears that concerns of coal oxidation were largely unfounded. I am aware of an experiment performed at Sandia, Livermore in which significant oxidation of pyrite was observed when coal samples were exposed to air over a period of about a week. However, it appears that the coal in the Sandia study was exposed to a steady stream of air. In contrast, the coal used in our study and in most studies was stored in a sealed drum prior to use. Therefore, only a limited amount of oxygen was available to oxidize the coal and pyrite. Based on our observations, oxidation of the pyrite in the coal does not appear to be a first order effect.

The large amount of unclassified material in the CCSEM analysis was of interest, especially since almost 25% of the iron was present in the unclassified category. Examination of the data points in this category showed particles consisting of Fe, S, Al, and Si. Some of the pyrite in the DOE coal is intimately associated with aluminosilicate minerals. Analysis of these intimately associated particles yields a "blend" composition that ends up in the unclassified bin. There were also other types of particles in the unclassified category that were either blends of known minerals or minerals which had not been included in our present classification scheme.

Routines to enable quantification of coal/mineral associations were also implemented this quarter on our new microanalysis system. We are currently testing these routines and should be able to report results next quarter. We have also added the ability to process data on-line for an analysis field so that we can return to a specific analysis point and verify our automated analysis of its composition and size. On line verification will be an important development tool as we refine our coal analysis and begin to examine associations in chars.

Task 2

The deposition probe design was tested and appeared to function well. Probe surface temperatures were kept in the temperature range appropriate for waterwall slagging and deposits were collected for about 45 minutes. A computer-controlled preheater for the overfire air was also added this quarter in order to better simulate the temperature profile experienced in large-scale boilers. Finally, an alarm system was added to alert the operators in the event of a flashback.

Task 3

The first deposit samples from the DOE Pittsburgh #8 coal were taken during the quarter. The deposits were formed while firing at three different stoichiometric ratios, 0.65, 0.75, and 1.04. All deposits were collected before the overfire air inlet. The stoichiometric ratio of 0.65 was intended to approximate the highly reducing environment initially experienced by particles in large-scale low NOx systems. Gas, coal and air flow rates were set so that the amount of oxygen added before the stage was approximately equal to that required to partially burn (to CO) all of the natural gas and the coal volatiles. Under these conditions there would be little oxygen left for char combustion and oxidation of char particles on the deposit surface. In contrast, oxygen is expected to be present at SR = 0.75 since the amount of oxygen which enters the reactor is more than sufficient to combust the volatiles.

Three distinctive types of deposits were formed. At SR=0.65, the deposit was black and consisted of char. This type of deposit is consistent with the low oxygen levels present under these experimental conditions. The deposit actually ignited and began to burn as it was removed from the reactor. At SR=0.75 the deposit was orange/gray and ash-like in appearance. Almost all of the carbon still present when the particles impacted on the surface was burned away in the deposit. Several millimeters of deposit accumulated during the 45 minutes of sample collection. However, the deposit appeared to be adhere loosely to the tube. At SR=1.04 significantly less deposit accumulated on the tube. However, the deposit appeared to adhere much more strongly to the tube than the SR=0.75 deposit, and appeared to have very little carbon. The difference in deposition behavior as a function of operating conditions will be an important focus of our work during the next quarter.

Task 4

The scanning electron microscope was used to analyze ash samples from the Pittsburgh #8 DOE coal which were collected during the previous quarter. Both manual and automated analyses were performed to examine particle morphology and mineral transformations.

SEM examination of the top sample collected at SR=0.65 revealed multiple cenospheric char structures which were largely intact. These chars contained ash, although the fraction of inorganic matter varied from particle to particle. Most of the ash in the char particles was molten, although the char appeared to restrict the coalescence of the included ash particles. Char structures were also observed in the sample below the staged air injection point at this stoichiometric ratio. However, the sample below appeared to have more spherical ash particles which were not associated with char. There was also more variation in the appearance of individual char particles which demonstrated different burning rates. Additional coalescence is expected as the char surface burns away and ash particles are brought together and have more time to coalesce. In fact, a related study indicated increased mixing of ash when a similar coal was burned in a drop-tube furnace under reducing conditions at a long residence time of 2.6 seconds[1]. However, the effect of air addition (staging) after 500 or 600 ms on ash coalescence has not yet been established.

Automated analysis of the samples was performed using a JSM 840A electron microscope and a Link ISIS microanalytical system. Samples were mounted in wax, cast into epoxy plugs, sectioned, polished and carbon-coated. Automated analyses were used to collect data from 2000 to 6000 inorganic particles, depending on the time available for analysis and the density of the particles in the sample. Sample analysis was performed at two magnifications.

The mineral phases in the coal which contained the largest proportion of sulfur were the iron sulfide phases. Therefore, sulfur release is directly related to the iron transformations and was examined as a function of firing conditions and sampling location. Figure 1 shows the frequency percent of iron containing particles as a function of their sulfur content (mole percent) for samples collected above the stage (top). A partial release of the sulfur above the stage was observed when firing at SR = 0.65 as pyrite mineral grains lose sulfur to form pyrrhotite. A peak in the frequency was observed in the mid-sulfur range, and the high-sulfur containing particles were no longer present. Considerably more sulfur was released after the stage (not shown). In contrast to the results at SR=0.65, almost all of the sulfur was released from samples collected above the stage (43cm) at SR = 0.75. Sulfur was also released when firing under conventional conditions (SR = 1.04), although more sulfur was present than at SR = 0.75. This is believed to be due to the longer residence time of the 0.75 sample.

The release of sulfur from iron containing particles is illustrated in a different form in Fig. 2 which shows particles for which the combined iron and sulfur was greater than 80%. Oxygen was not measured so that particles which approach 100% iron are really iron oxide. Note the group of particles in the coal whose composition is approximately 30 mole% iron and 60 mole% sulfur, corresponding to pyrite. The particles lose sulfur in the combustor and their compositions shift down and to the right as shown on the figure. The rate of sulfur release varies from particle to particle as evidenced by the distribution of sulfur in the partially oxidized particles. The difference in the release rate was a function of particle size is shown in Fig. 3. These results indicate that the larger particles are more readily oxidized than the smaller particles. It is likely that the oxidation rate depends on whether the individual pyrite grains are included or excluded. Therefore, the results in Fig. 3 may reflect a correlation between particle size and the likelihood of a particle being included or excluded.

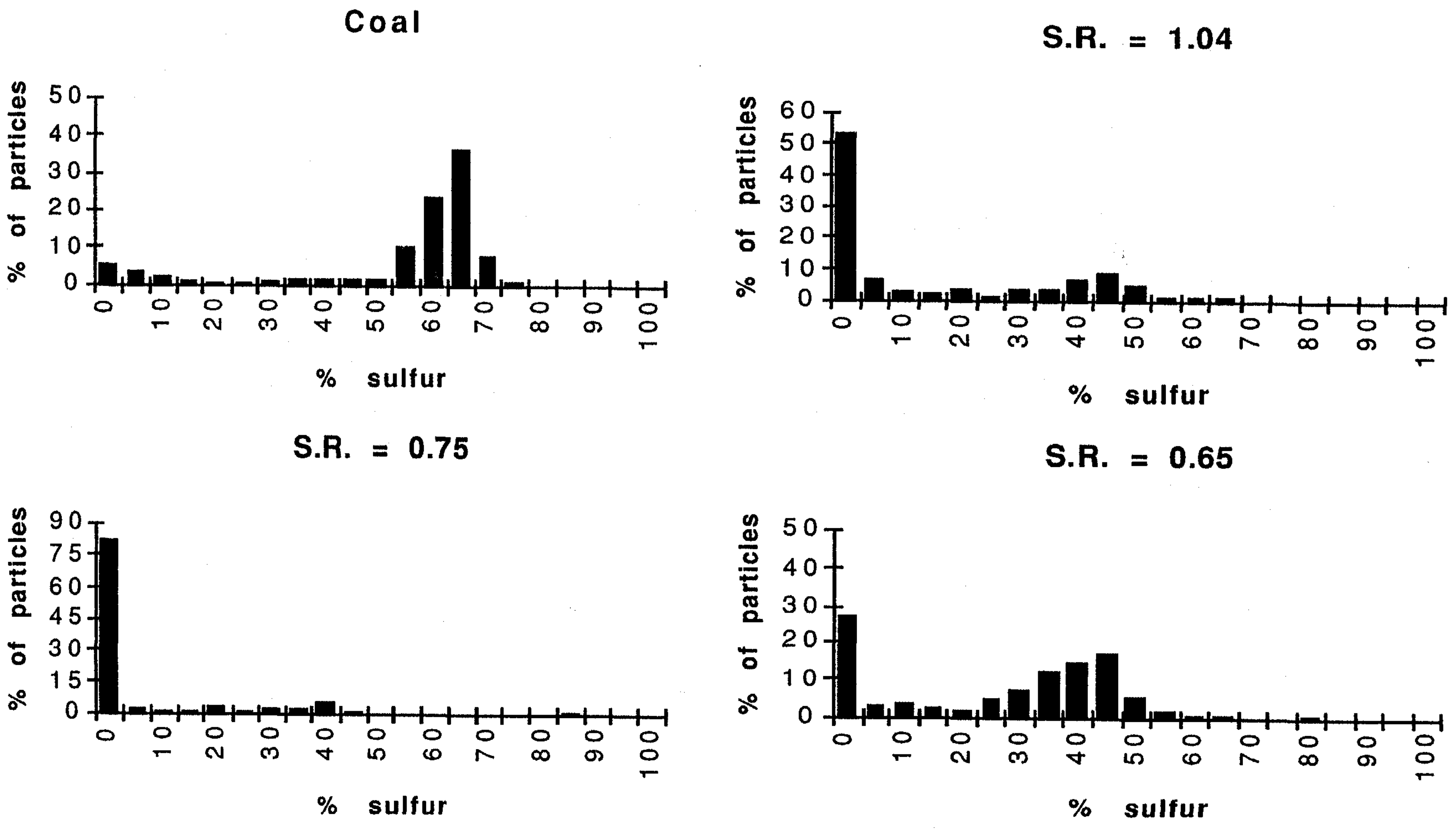

Figure 1: Percent sulfur in Pittsburgh #8 coal and char particles

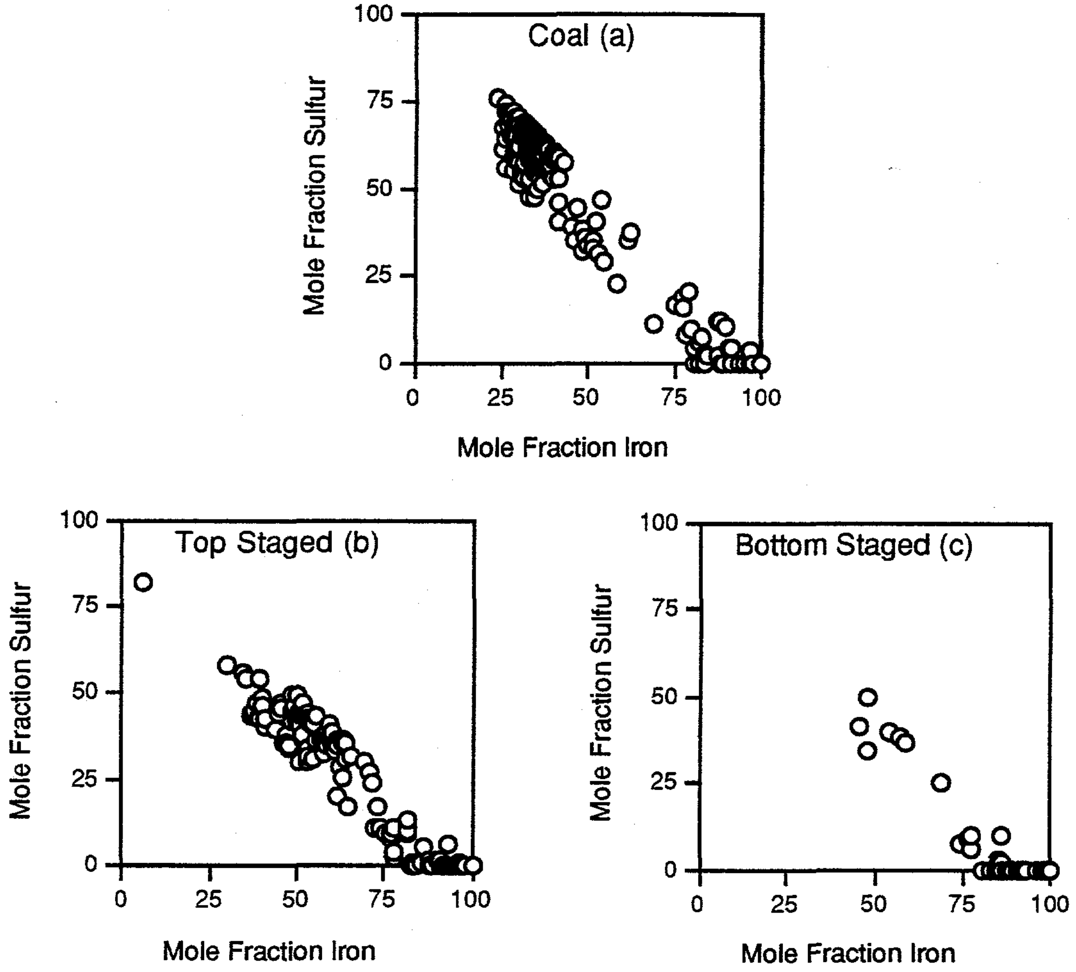

Figure 2. Iron and sulfur content of individual particles containing greater than 80% Fe+S (oxygen excluded): a) coal, b) top sample collected 43 cm from the burner under staged conditions, c) bottom sample collected 107 cm from the burner after staged-air addition.

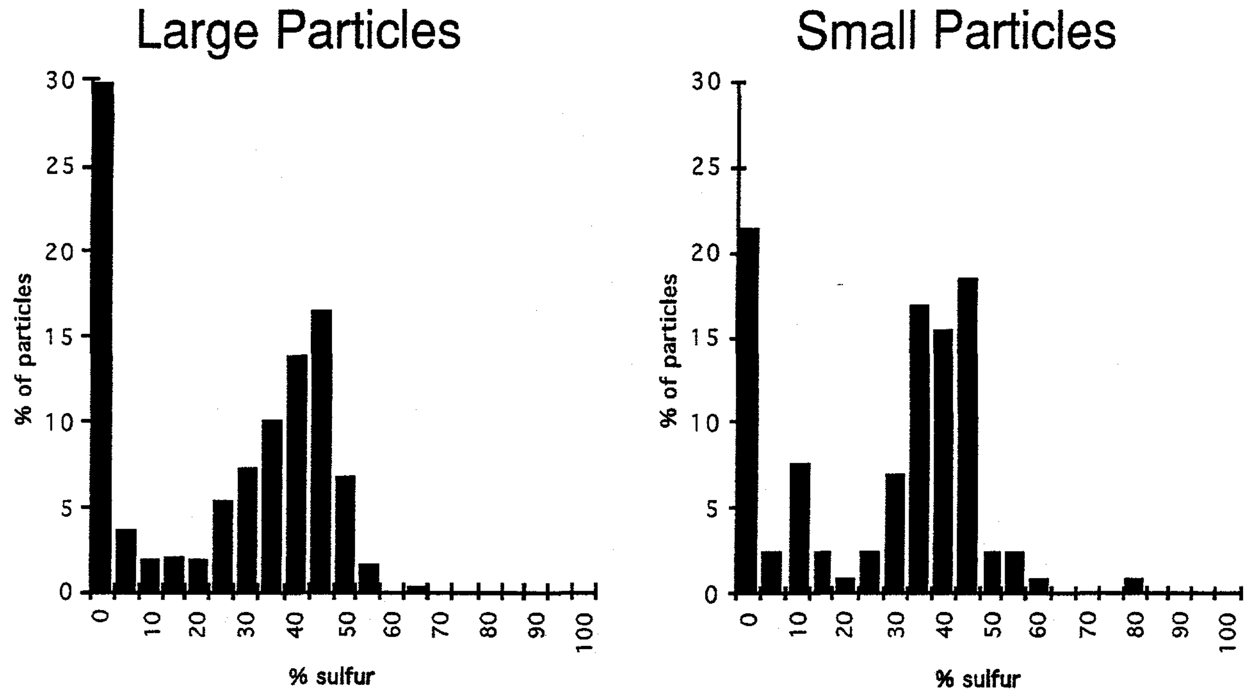

Figure 3: Comparison of sulfur release in large and small particles

Sulfur release from iron sulfide particles is important because these particles melt and may remain in a molten phase until oxidation is complete and only iron oxide remains [2]. The delay in oxidation caused by staged combustion creates the potential for the molten phase to persist longer in the combustor. However, the delay only appears to be important at the lowest stoichiometric ratios. Molten particles which are not associated with the char are more likely to stick to heat transfer surfaces and promote deposition. In contrast, molten particles included within char particles may be physically impeded from contacting the heat transfer surface and therefore may not contribute to increased deposition. However, the molten iron oxysulfide particles within the char may coalesce with other particles during char combustion to change the ash/deposit chemistry.

The large extent of pyrite oxidation at SR=0.75 was unexpected and indicates that the these particles may be preferentially oxidized, or that a gas phase species other than oxygen may contribute to the oxidation. However, the oxidation state of the resulting iron oxide is not known and it is possible that the iron remained in a lower oxidation state.

The nature of these iron transformations as well as transformations of other particles will be examined as part of continuing work on this project.

References

1. J.J. Helble, Fundamental Study of Ash Formation and Deposition: Effect of Reducing Stoichiometry, Quarterly Report #5 PSI-1178, Prepared for the U.S. Department of Energy. (1994)
2. S. Srinivasachar and A.A. Boni, Fuel 68 (1989) 829.

D. Plans for the Next Quarter

1. Examine the behavior of included and excluded minerals and ash under a variety of operating conditions, with particular attention on the behavior of included pyrite.
2. Continue development of CCSEM routines to permit association analysis on coal and char.
3. Continue parametric testing for particulate samples on both the Black Thunder and Pittsburgh coals.
4. Perform a series of deposition tests on both coals and correlate observed deposition behavior, ash chemistry, deposit chemistry, and operating conditions.