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**INVESTIGATION OF MINERAL TRANSFORMATIONS AND ASH DEPOSITION
DURING STAGED COMBUSTION**

Quarterly Technical Progress Report
April 1, 1996 to June 30, 1996

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FOREWORD

This report summarizes technical progress during the eleventh quarter (April 1, 1996 to June 30, 1996) of a 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 Peter Slater and Neal Adair. Eyas Hmouz, and John Dobbs, undergraduate students in chemical engineering at BYU, also made important technical contributions to this report.

ABSTRACT

This report describes work completed during the eleventh quarter of a DOE-funded study of mineral transformations and ash deposition during staged combustion. Accomplishments included repairs and improvements to the laboratory combustor, collection of deposits and observation of deposition behavior as a function of operating conditions, and analysis of deposit samples collected under both staged and conventional conditions.

The water cooling shell for the brass burner was rebuilt this quarter. It was necessary to rebuild the cooling shell because of frequently occurring leaks which could no longer be repaired. No new leaks have occurred since the repairs were made.

Deposits were collected for several stoichiometries between $SR=0.65$ and $SR=0.75$. A changeover from carbon-rich deposits to deposits which contained little carbon was observed at about $SR=0.73$ for the coal and natural gas feed rates used the experiments. However, even deposits which contained relatively little carbon had a carbon-enriched layer at the tube surface. This layer was due to carbon which did not burn out completely after impaction. A similar type of carbon layer may affect deposit formation in utility boilers.

One of the key contributions this quarter was the analysis of deposit samples collected under both staged and conventional conditions. These initial results indicate that deposits formed during staged combustion of a Pittsburgh #8 are similar to those formed during conventional combustion. Some small differences were observed and it is not yet known how significant these differences may be. However, substantial differences between the deposits and ash samples were observed. These differences were apparent in both the bulk compositions and "species" distributions. Continuing work will focus on clarifying and quantifying the effect of staged combustion on deposit formation and strength development.

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 NO_x emissions from coal-fired units. It is applicable to both advanced combustion systems currently under development (e.g. HITAF) and low NO_x retrofits for existing units. These low NO_x 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 eleventh 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 eleventh quarter. Progress is summarized by task.

Task 1

As mentioned above, the purpose of this task was to select specific coals, prepare the coals for use in the laboratory combustor, and perform a detailed characterization of samples from the prepared coals. This task has been largely completed and no additional work on this task was performed during the quarter.

Task 2

The purpose of this task was to prepare and test reactor facilities and sampling probes for use in the current experimental program. This testing has been largely completed, although improvements and maintenance work continue. This quarter it was necessary to replace the tubes used to supply cooling water to the burner. A schematic of the burner is shown in Figure 1. The tube assembly consists of small tubes connected with silver soldered joints to a common inlet and outlet tube. Leaks tend to occur at the joints over a period of time because of thermal stress on the tubes. These leaks are normally repaired by re-soldering the joint. However, it was no longer possible to adequately patch the frequently occurring leaks since most of the tubes had been re-silver soldered at least once since construction. Therefore, all of the tubes were removed and replaced with new tubes of the same size. No further water leaks have occurred since the tubes were replaced.

Task 3

During this quarter, additional deposit samples were collected for the DOE Pittsburgh #8 coal. An improved experimental procedure was also established in order to overcome problems observed previously. Experiments were performed for several different stoichiometries ranging from $SR=0.65$ to $SR=0.75$. For these tests, 2 lb/hr (23,800 BTU/hr) of coal was fed. The total rate of energy (BTU/hr) was the same for all of the tests (40,500 BTU/hr).

Deposits were collected at a single sampling point located 43 cm from the burner. A significant difference in the types of deposits formed was observed over the range of stoichiometric conditions considered. The deposit formed at the lowest stoichiometric ratio of $SR=0.65$ was black and consisted mostly of carbon. The deposit ignited when removed from the combustor, indicating low O_2 levels in the combustion chamber. In contrast, deposits formed at $SR=0.75$ contained relatively little carbon. At this stoichiometric ratio, there was sufficient oxygen in the stream to burn out the char after it had impacted on the wall. Tests at intermediate stoichiometric ratios indicated that the changeover point from carbon-rich deposits to deposits

which contained only small amounts of carbon occurred at about $SR=0.73$. This changeover is a function of the gas and coal feed rates and cannot be extrapolated to large utility-scale systems. However, the results indicate that only small amounts of oxygen are needed to burn out carbon on the wall. The temperature of the deposit was also an important factor which influenced carbon burning on the wall. In particular, particles at the cool tube surface did not burn out completely after impacting on the surface. Therefore, a significant amount of carbon was present in the deposit adjacent to the tube, resulting in a deposit which was only loosely attached to the tube. It is possible that a similar type of layer may affect deposit formation in utility boilers.

Two key issues relevant to this study are: 1) the effect of staged combustion on deposit formation, and 2) the effect of the local stoichiometric ratio on the sintering and strength development of deposits. Consequently, a test plan was developed this quarter in order to address these issues. Deposits will be grown under both oxidizing and reducing conditions at, for example, $SR=0.75$ and $SR=1.04$. After a deposit has been grown for 45 minutes, the coal will be turned off and the deposit will be cured in the combustor fired by natural gas alone. Curing will take place for about two hours under either oxidizing or reducing conditions. This means that, for example, two deposits will be grown at $SR=0.75$. One of these deposits will be cured at $SR=0.75$, and the other will be cured at $SR=1.04$. A similar curing will be performed for two deposits grown at $SR=1.04$. These experiments should provide insight into the effects of staged combustion on deposit formation and sintering. The test plan will be carried out during the next quarter, along with the corresponding analyses.

Task 4

The scanning electron microscope was used to conduct an analysis of previously collected deposit samples. The samples analyzed were deposits collected at $SR=0.75$ and $SR=1.04$ with a heating rate of 80,500 BTU/hr. Figure 2 is a backscattered electron image of the $SR=0.75$ deposit which provides evidence that some sintering of the deposit has occurred.

Automated point count analysis (SEMPC) was performed on these samples using a JSM 840A electron microscope and a Link ISIS microanalytical system. The deposits were mounted in epoxy, cross-sectioned, polished and carbon-coated. Sample analysis was performed at a magnification of 250X on a 20 x 16 grid. The number of points at which analytical data were collected was 1242 for the $SR=0.75$ sample and 2328 points for the $SR=1.04$ sample.

A comparison of the bulk composition of the deposits determined from SEMPC with that of the ash and coal is shown in Table 1. All ash and deposit samples in the table were collected at the same location (43 cm from burner). As can be seen from the data, the bulk compositions of the deposits are similar to each other but are different from the coal and ash. Specifically, the deposits are enriched in iron and depleted in silica, alumina, and sulfur relative to the ash and coal. This enrichment is consistent with selective deposition of iron-containing particles.

Table 1. Comparison of Oxide Weight Percents in Coal, Ash, and Deposits.

Oxide Wt %	Coal	0.75 Ash	1.04 Ash	0.75 Deposit	1.04 Deposit
SiO ₂	48.09	47.56	49.59	44.20	43.18
Al ₂ O ₃	21.89	21.88	24.58	18.19	18.63
Fe ₂ O ₃	18.10	17.11	12.17	27.58	29.99
CaO	6.72	5.38	4.96	6.97	5.20
SO ₃	2.27	2.71	3.67	0.17	0.22
K ₂ O	1.74	1.80	1.89	1.65	1.66
MgO	1.16	0.89	0.88	0.37	0.36
TiO ₂	1.06	0.96	0.77	0.33	0.35
Na ₂ O	0.75	0.63	0.57	0.41	0.29
P ₂ O ₅	0.38	0.62	0.52	0.11	0.06

Figure 3 shows a comparison of the distributions of different chemical species in the ash and deposit samples. As seen in this figure, the deposits contained a lower percentage of kaolinite than the ash. The deposits were also enriched in Ca-Al-Silicate and Fe-Silicate phases. Additionally, the deposits had significantly more composition points that were unclassifiable. These results indicate that a substantial amount of sintering and mixing had occurred in the deposits, in spite of the fact that they were relatively thin and had only been allowed to grow for 45 minutes (with no curing).

Figure 3 also shows that the composition of the deposits formed at different stoichiometric ratios were very similar. The similarities between these samples are also evident in Figs. 4 and 5 which are ternary Fe-Al-Si diagrams. These figures display all of the analysis points where the combined amount of iron, aluminum, and silicon was greater than 80% on an oxygen free basis; most of the analysis points for both samples satisfied this criterion and are shown on the diagrams. Similar data for the ash are provided in Figs. 6 and 7. A comparison of Figs. 4 and 5 with Figs. 6 and 7 once again illustrates significant differences between deposit and ash samples. For example, the ash diagrams show that a large fraction of the ash consisted of particles derived from kaolinite (~50% Si, 50% Al). In contrast, the fraction of kaolinite-derived material in the deposits was significantly less. One explanation for this observation is that the kaolinite derived particles are less likely to stick to the surface. On the other hand, the decreased amount of kaolinite in the deposit samples may also be due to the sintering of particles to yield blended compositions. The relative importance of these two processes will be investigated as part of this study. Note, however, that the deposit morphology, phase distribution data and the ternary diagrams indicate considerable blending in the deposits relative to the ash.

Finally, an analysis of the unclassified points in the deposit data also revealed similarities

between the two deposit samples. The unclassified points were grouped with the new classification algorithm developed as part of this study. This analysis showed that even the unclassified points in the two deposit samples were similar.

The above results indicate that staged combustion did not dramatically affect deposit formation from the Pittsburgh #8 coal. Some differences, however, were observed as evident in Fig. 3. The significance of these differences will be explored in continuing work. The test plan developed this quarter should allow us to further characterize and quantify the effect of staged combustion on deposition formation and strength development.

D. Plans for the Next Quarter

1. To carry out the test plan described above (see Task 3) in order to further characterize the effect on staged combustion on deposits from the Pittsburgh #8 coal.
2. Analyze the deposit samples collected from these tests and quantify the affect of staged combustion on deposition from the Pittsburgh coal.
3. Analyze Black Thunder ash samples and determine the effect of staged combustion on ash formation. Analyses will be similar to those used for the Pittsburgh #8 coal.
4. Collect and analyze deposit samples from the Black Thunder coal.

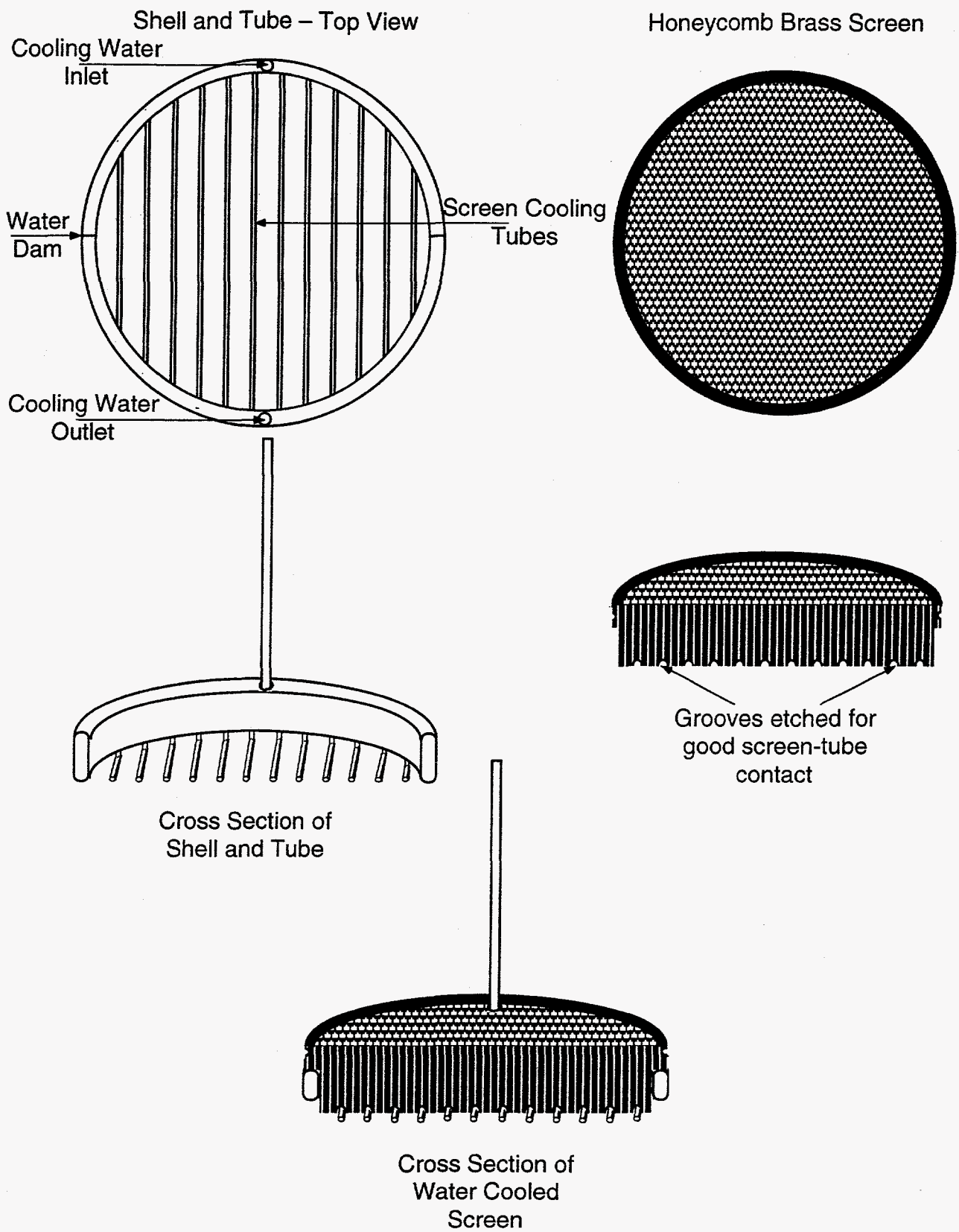


Figure 1. Water cooled burner design

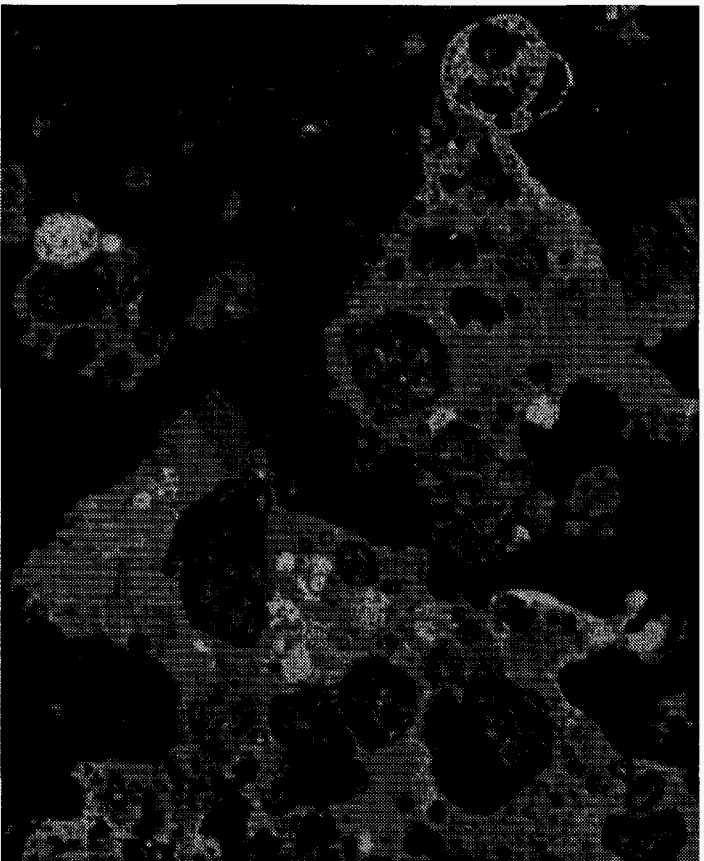


Figure 2. Backscattered electron image of SR=0.75 Deposit

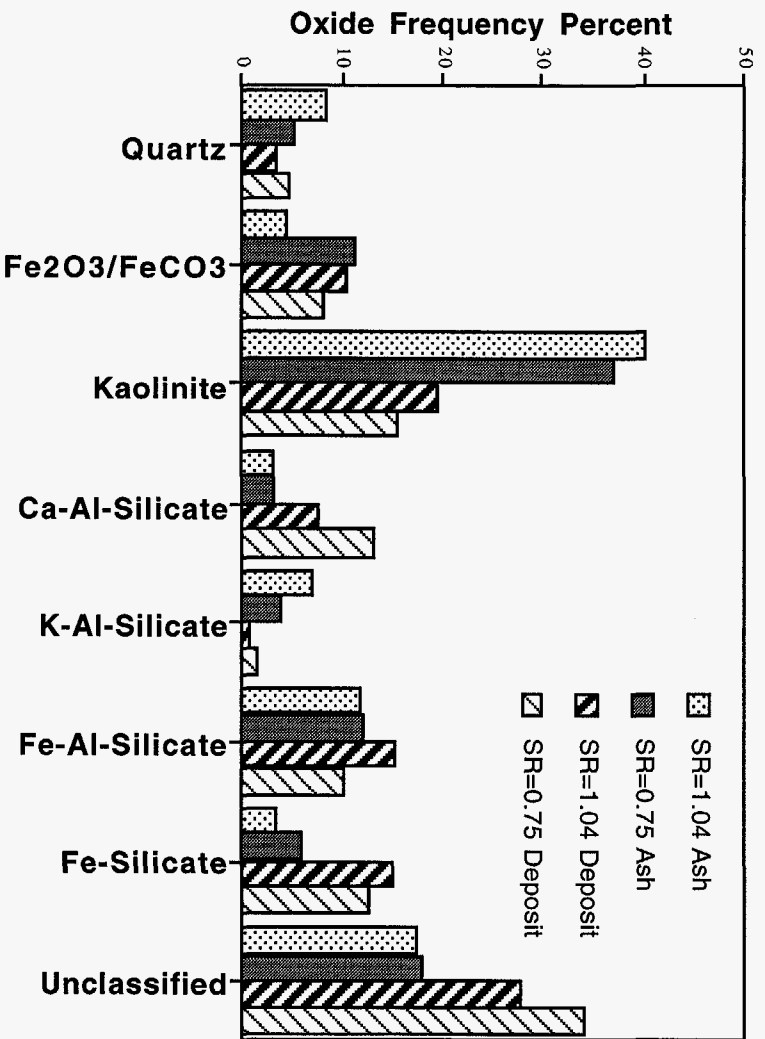


Figure 3. Comparison of ash and deposit major phase distribution

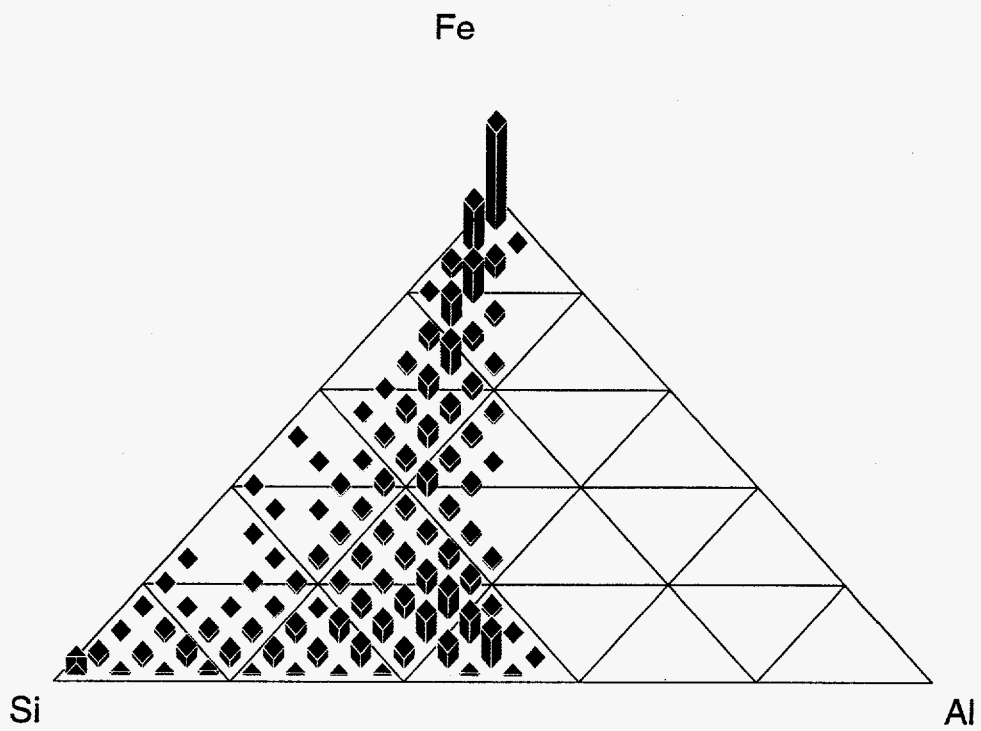


Figure 4. Ternary diagram of SR=0.75 deposit

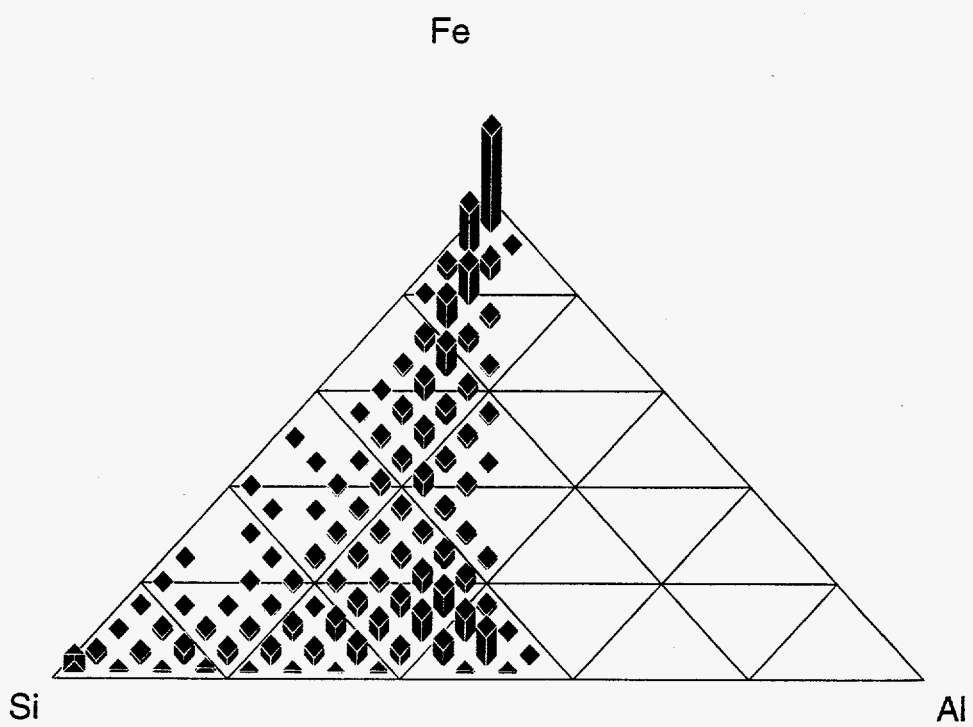


Figure 5. Ternary diagram of SR=1.04 deposit