

## DEPOSIT REMEDIATION IN COAL-FIRED GAS TURBINES THROUGH THE USE OF ADDITIVES

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### ABSTRACT

Deposit formation represents a key impediment to the eventual commercialization of a direct coal-fired gas turbine engine. Deposits result from the thermal decomposition of coal-borne mineral matter followed by impact and adhesion along the hot gas pathway.

One strategy for deposit abatement is hot gas cleanup to remove particulate before entering the turbine. An alternative strategy, described in this Paper, is to modify the mineral matter/ash chemistry to render it non-adherent through the use of additives. In this way, the complexity and expense of hot gas cleanup is obviated. To date, alumina, boehmite, and a variety of kaolin clay additives have been tested in a coal-water mixture fired gas turbine simulator. A washed kaolin clay has proved to be most effective in reducing airfoil deposition. A mechanism involving in-situ slag decomposition, exsolution, and spontaneous spalling is proposed.

### INTRODUCTION

A key objective of the Advanced Coal Fueled Gas Turbine Systems Program, a U.S. Department of Energy initiative, is to develop the technological basis necessary for subsequent commercial development of a direct-fired gas turbine power system. The system concept described in this paper uses a GE LM500 advanced aeroderivative gas turbine engine designed for direct firing of coal fuel. This system can be used in transportation and small stationary power applications. Components and systems required to achieve this objective in a cost-effective and environmentally sound manner are being developed.

Previous work Ref. 1-6, 9-16, reported in the open literature indicates that deposition represents a potential impediment to the commercialization of the coal-fueled gas turbine. Deposits reduce engine efficiency, and require potentially costly maintenance and down-time. Deposition is a prerequisite to hot corrosion (France, 1984).

In order to eliminate deposition, one or more of the key steps in deposition process must be interrupted. These steps are potentially system and fuel dependent, representing the complex interplay of fluid mechanics and thermochemistry.

In general, deposition can be considered as a sequence of events consisting of particle arrival and adherence. Potential mechanisms have been reviewed (Ref. 1). Applicable mechanisms for the in-line annular combustion system are the subject of this investigation, and are probably unrelated to off-board slagging systems (Ref. 2) which have distinctly different time/temperature/flow profiles, and where pre-expansion ash/slag removal is under investigation.

In order to minimize ash particle arrival rates, coal is micronized to comminute mineral matter deposit precursors, and is beneficiated to reduce the overall quantity of ash present in the system. Mineral matter occurs in coal as finely disseminated grains which melt during combustion. Presumably, if there is less mineral matter in the coal, there will be less to adhere. Complete de-ashing of the coal is not yet economically feasible. By micronizing the coal, mineral grains are also comminuted. Finer ash particles are more likely to follow hot gas path streamlines (Ref 16) and avoid impaction on the airfoils. Other mechanisms for deposition of fine particles are applicable (Ref. 8). Much of the ash remains weakly adhered to unburned char surfaces which results in larger effective Stokes diameters and impaction tendencies. To the extent that good atomization and

combustion efficiencies are achieved, this will be minimized.

Once the particles approach the airfoil surfaces, they can undergo collisional impact. To adhere, the particle kinetic energy must be at least partially dissipated, or it will not stick. By cooling the target, the molten slag which comprises the ash will freeze in the boundary layer, greatly reducing its stickiness and tendency for inelastic adhesion.

Unburned carbon will have a deleterious effect on the deposition tendency of the ash, reducing its melting point and also generating heat even after deposition. Unburned carbon has not been detected in deposits, but samples obtained by quenching combustion products (figure 1) reveal 10-40% of the combustion products consist of unburned carbon, even for combustion efficiencies in excess of 99.5%. Presumably final burnout takes place on the airfoil surface. In addition, carbon shell fragmentation may serve to dissipate particle translational energy. Improved burnout and reduced shell size are desirable, and are enhanced by improved atomization of slurry (Staub, 1988).

The condition of the target surface will also influence deposition. If it is cold and clean, there will be a limited tendency for inelastic collisions by the ash. If it is covered with a porous and fluffy surface, collisions may collapse the suprastructure and increase deposition. A very weak deposit may be eroded by incoming combustion products. A viscous liquid on the surface will very efficiently capture particles. In the event of extreme viscosity, the capture may be reduced as the surface may appear to be solid to the products of combustion.

Once deposited, the particles can be re-entrained by erosion, or may be sintered or even completely fused into a liquid. Kuczynski (Ref. 7) showed that sintering of glassy particles is governed by viscous flow. Deposit chemistry and temperature (Ref. 8) therefore determine sintering rate. A weakly sintered deposit initially develops which is subject to erosion or on-line abrasive cleaning, but eventually will fuse to a tenaciously adherent mass.

By understanding the chemistry and mechanism of deposition, the best means for deposit prevention or remediation may be identified.

## EXPERIMENTAL

Coal-water mixture was provided as a 50% slurry by Otisca Industries. A summary of the slurry properties appears in Table 1. For the first four kaolin tests, an air classified kaolin was used in both a dry powder and a 70% slurry form. The dry powder was slurred with water and Colloid 211 sodium polyacrylate surfactant. Kaolin slurry was added slowly with stirring to pre-mixed coal slurry, and stirred for 1 hr. prior to combustion. The amount of kaolin was 0.8% by weight of dry coal. The kaolin contained mostly kaolinite with traces of anatase (TiO<sub>2</sub>). Atomic absorption spectroscopy also revealed 1000ppm sodium on a slurry basis with comparable amounts of potassium anticipated.

Analytical data on deposits (vide infra) suggested that sodium was responsible for the more severe deposition. In order to limit its participation, a highly beneficiated kaolin, Satintone V\* was used. It has a mean particle diameter of 0.8 microns and was mixed as a 46% slurry with Colloid 111 ammonium polyacrylate surfactant. Centrifugation of the slurry at 7000 rpm for 2 hr yielded a supernatant liquor with soluble sodium content of 2.8 ppm as determined by inductively coupled plasma emission spectroscopy. Thus the impact of alkali in such low concentrations could be minimized.

Alpha alumina, Alcan A16SG was also employed as an additive, with a primary particle size of 0.5 microns, and a surface area of 8.229 meters squared/gram. The alumina was dispersed with either Colloid 211 sodium polyacrylate, or Darvan C polyelectrolyte.

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Boehmite has the formula  $\text{AlO}(\text{OH})$ , occurring in the gamma orthorhombic form. It has true density of 3 g/cc, and a hardness of 3.5-4 on Moh's scale, or roughly that of calcite. It is available in ultrapure form (no detectable alkali) as a byproduct of the Ziegler process for making alpha-olefins and fatty alcohols.

The actual boehmite used in the testing was Catapal A, a dry flowable powder which consists of 30-50 angstrom boehmite crystals which had been spray-dried to 30-50 micron granules. While complete dispersion of the crystals is possible under mildly acidic conditions, it was deemed undesirable since complete dispersions greater than 2% by weight will gel. On the other hand, the as-received grains were considered to be too coarse, representing a potential source of erosion in the event that sintering took place in the gas stream. However unlikely this might seem, precautionary comminution was performed in a mullite lined dry ball mill, using a charge of 50% volume 1" cylindrical alumina media for not less than 24 hrs. Sedimentation equivalent spherical diameter of the milled grains had a mean of 0.6 microns, considered to represent an acceptable risk of erosion, as was borne out.

Slurry was burned in the turbine simulator with no special measure taken to accommodate the presence of additives. Numerous combustion trials with doped slurry were made over a period of several months, with a typical test duration of 4-30 hr. Test conditions included the LM500 simulator, Figure 2, a 2000F firing temperature, a chamber pressure of 130 psig and the atomizing air pressure ratio maintained at 1.9. Oil assist was set at 10% to minimize complications due to combustion instability. In actuality, combustion instability did occur in the initial testing due to excessive atomizing air temperature, but this was corrected at the latter stages of testing.

Deposition rates are obtained on line through the determination of Normalized Nozzle Area Index Number (NAIN). NAIN is an indirect measure of the critical throat area between the airfoils. As deposits build up, the throat area is reduced, effectively reducing the mass flow at constant chamber pressure and temperature. By directly measuring these parameters, the NAIN can be calculated (Kimura, 1987).

## RESULTS AND DISCUSSION

In the absence of additives, deposit formation is initially high, and after 25-40 hr, becomes catastrophic. (References) Figure 3 shows deposits from untreated Blue Gem coal after 20 and 45 hr respectively. In order to explore the concept of deposit remediation through ash modification in coal-fired gas turbines, several tests employing inorganic additives to Blue gem coal slurry were performed. The Blue Gem coal is highly slagging, dominated by the considerable presence of iron and calcium, Table 1.

### ALUMINA ADDITIVES

Alumina, Alcan A16SG 0.5 micron mass mean diameter, was added to as an aqueous dispersion to the coal slurry in an amount sufficient to double the total ash content of the fuel. Considerable care was taken to ensure that the alumina was not agglomerated in the dispersion. Combustion of the alumina-doped slurry took place for 13 hrs in the turbine simulator. During the test, the NAIN actually increased by 2%, as compared to an anticipated reduction of 2-3% for an untreated coal. The obvious implication was that erosion was occurring which was opening the critical throat region.

The test was halted after 13 hr, and the airfoils were visually inspected. Pressure side and leading edge deposits were found to be considerably less than previously obtained despite the much higher ash loading. The deposits were whitish in appearance and were only slightly fused. Signs of erosion were apparent on both the airfoils and end walls. The vane trailing edge surface had become eroded to nearly a knife edge, and bare metal was obvious along the pressure side surface. The system was reassembled and refired on oil followed by nutshelling. The abrasive injection removed virtually all leading edge and pressure side deposits, confirming the efficacy of altering ash chemistry.

The system was refired on alumina-doped coal slurry for an additional 10 hours, with reduced alumina content, now 0.5 of the indigenous 0.8% ash content. The qualitative results were identical to those observed during the initial test segment.

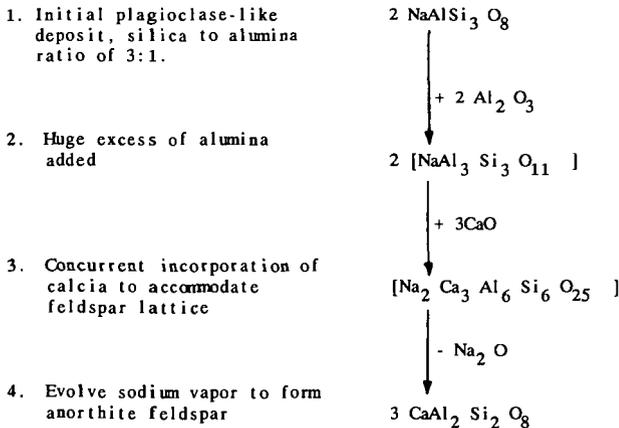
The conclusion from the alumina-added test was that indeed ash modification could take place by judicious addition of inorganic species, but that care must be taken to ensure that erosion did not occur.

## BOEHMITE ADDITION

Based on the alumina test results, showing reduced ash adhesion accompanied by unacceptable erosion, boehmite was selected as an alternative. Boehmite is a hydrous alumina  $\text{AlO}(\text{OH})$ , isostructural with lepidochrosite. Its hardness is ca. 3.5 on Moh's scale, as compared to 9 for sapphire. Thus its erosive tendency should be greatly reduced. Further, it is available in extreme purity as a byproduct from the Ziegler process for alpha-olefin synthesis which employs triethylaluminum. The byproduct fume has an inherent particle size range in the tens of angstroms, and can be dispersed in acidic media. However, to avoid the potential for gelling, spray dried clusters 30 microns in diameter were obtained and dry-ball-milled to 0.6 microns. A slurry was prepared without dispersant, and was admixed with the coal slurry in sufficient quantity to equal the amount of indigenous ash in the coal.

The coal was burned, as usual, in the LM500 turbine simulator for a period of six hours. In contrast to the alumina test, deposition was observed with a NAIN reduction of over 1%. Large chunks formed in the transition section and on the leading edge of the airfoils, and a fine powdery adhered to the suction surfaces.

Analysis of the deposits revealed the usual complement of phases including anorthite, anhydrite, vuggy mullite crystals lining the pores, alpha alumina, hematite, and glass. Not anticipated was the presence of alkali sulfates, which we suggest arose from the following sequence:



The driving force for these reactions is to incorporate as much of the alumina into the feldspar lattice, which is also benefited by the evolution of alkali. The Si/Al ratio starts at 3/1 and ends at 1/1 as is observed. It is the evolution of alkali which results in alkali sulfate glue formation and deposition. In essence, the alumina reversed the gettingter process.

If this interpretation is correct, the use of alumina as a deposition control additive is fundamentally incorrect; it will exacerbate deposition in all but the most silica-rich deposits.

## KAOLIN ADDITIVES

Kaolin clay was added, again in an amount sufficient to match the indigenous ash content of the coal. Four tests ranging from 6 to 15 hr in duration were performed using an air classified kaolin clay. Deposition on the airfoil surfaces was minimal, though upstream in the transition section leading to the

airfoils, chunks had formed which occasionally spalled and wedges in the turbine throats. Analysis of these deposits revealed a ten-fold enrichment of alkali metals in the deposit, presumably resulting from alkali impurities in the clay and the sodium polyacrylate surfactant. By using a highly beneficiated clay and an ammonium polyacrylate surfactant, the upstream deposition was considerably diminished. Comparison between deposits from the untreated coal (Figure 3) and the kaolin-treated coal (Figure 4) demonstrate clearly that it is the ash chemistry which dominates the deposition process, rather than the ash quantity.

In order to take full advantage of Kaolin for deposit mitigation, a method for eliminating formation of chunks of deposits which form in the transition piece must be identified. It is expected that through proper thermal and aerodynamic design, this will be accomplished.

It is speculated that the function of the kaolin is two-fold. First, it acts as a network extender, raising the viscosity and surface tension of the melt on the airfoils. Second, it shifts the composition of the melt from the anorthite phase field into the mullite phase field. Exsolution of the high density mullite results in pore formation, especially along the deposit/airfoil interface. The net effect is to reduce the contact area between the deposit and the airfoils so that the ash will either spontaneously spall or erode. Analytical and microscopic evidence supports this hypothesis.

#### SUMMARY

Deposit formation represents a key impediment to the commercialization of coal-fired gas turbines. It was determined that addition of judicious amounts of ash modifiers, especially inexpensive kaolin clays, is an effective means to render the ash non-adherent.

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Table 1- Properties of Otisca Coal-Water Mixture

PROXIMATE ANALYSIS (Dry Basis)		ASH ANALYSIS	
Ash Content %	0.90	SiO <sub>2</sub>	22.4
Total Sulfur %	0.80	Al <sub>2</sub> O <sub>3</sub>	29.15
Volatile %	37.92	TiO <sub>2</sub>	1.80
Fixed Carbon %	61.18	Fe <sub>2</sub> O <sub>3</sub>	28.54
Solids %	49.87	CaO	9.86
Viscosity cp (112/sec)	270	MgO	3.00
		K <sub>2</sub> O	0.17
		Na <sub>2</sub> O	0.54
		SO <sub>3</sub>	0.62
		P <sub>2</sub> O <sub>5</sub>	0.33
		SrO	1.09
		BaO	0.67
		MnO	0.04

PARTICLE SIZE DISTRIBUTION

Diameter	Mass %
> 11.5	7.0
11.5	0.5
10.5	0.0
9.5	4.0
8.5	4.4
7.5	3.2
6.5	6.2
5.5	7.6
4.5	10.8
3.5	14.0
2.5	18.4
1.5	18.5
0.5	5.4

ASH FUSION DATA

	Reducing	Oxidizing
Initial Def	2215	2470
Softening	2415	2545
Hemispherical	2535	2605
Fluid	2655	2655

D50= 3.55 micron

Figure 1- Quench probe samples show char cenospheres, fume, and frozen slag spheres.

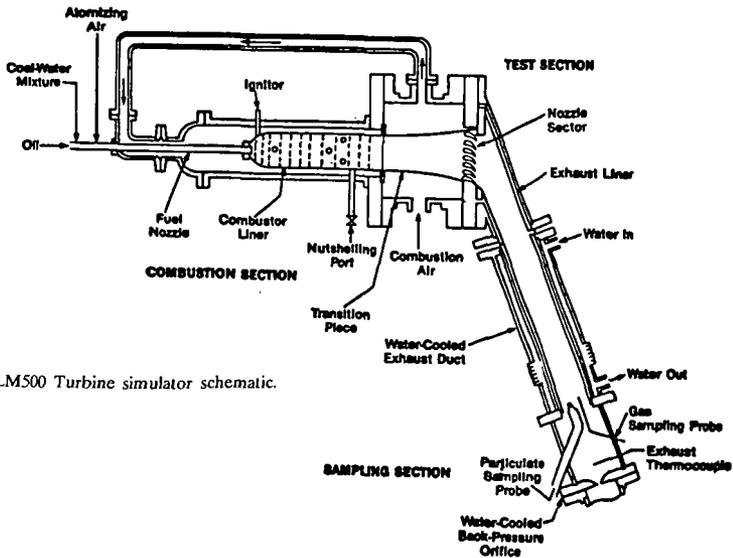
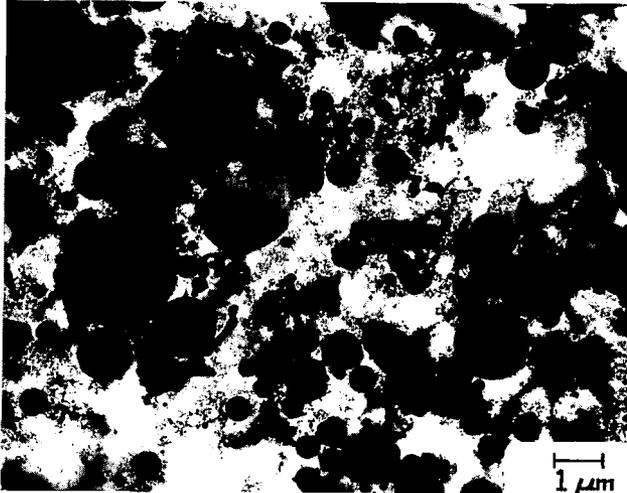


Figure 2- LM500 Turbine simulator schematic.



Figure 3- Comparison of deposition before and after treatment with kaolin additive.

