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FIRESIDE CORROSION IN MUNICIPAL WASTE FIRED SYSTEMS

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INTRODUCTION

Corrosion of heat transfer surfaces in municipal waste-to-energy (WTE) systems is a major concern to the designers and operators of such systems. Indeed, extensive effort is made on the design, fabrication, and operation of such units to minimize forced outages caused by corrosion-related boiler tube failures (BTF's). These aspects include the maintenance of lower metal temperatures than that used in comparable biomass or fossil-fired systems. For water-wall surfaces shielding or cladding is routinely used to protect the carbon steel tubes. Shielding options include silicon carbide refractory or other appropriate types of refractory. Cladding of the tubes with weld overlay material is also used to a great extent. Operating factors to minimize corrosion includes careful control of firing rate and attempts to maintain an oxidizing atmosphere at the heat transfer surfaces.

While these protective methods have their uses they do not address the true root cause of the corrosion process. Indeed, there has been little extensive study of fireside corrosion in WTE systems and the influence of operating and design parameters on the processes. This is not surprising given the complexity and variability of the fuel and the different design and operating configurations. The development of root cause analysis is also difficult with the reluctance of the operators of many units to undertake the detailed procedural program required. A reason for this is that the owner/operators have not determined the return on investment of such programs. However, rigorous failure analysis programs such as the boiler tube failure reduction project established and supported by the Electric Power Research Institute have resulted in significant lowering of forced outage rates due to boiler tube failures.

In order to understand the corrosion mechanism on heat transfer surfaces it is necessary to establish a framework or model of the process involved in a WTE systems and what occurs in such systems which leads to corrosion or wastage. In general the WTE takes garbage or refuse derived fuel and burns the material on a grate. The design and operation of grates is based on the characteristics of the fuel and tends to be proprietary technology supplied by different original equipment manufacturers. The grate system transports the fuel to the furnace where excess air is added and the fuel is designed to burn. Due to the various densities of the feedstock, some material will remain on the grate and be carried out of the furnace, some dense fine material will fall through the grate into an appropriate hopper. The less dense fuel will be elutriated from the grate and transported into the furnace to be burnt in suspension. This material includes paper, plastics, small particles of woods, etc. Therefore, the actual ash which is formed in WTE systems and conveyed to the heat transfer surfaces is somewhat dependent on the design of the system, the operating conditions and the fuel characteristics. The ash formed can deposit on the surfaces and initiate as well as facilitate the corrosion process.

A recent study has shown the complexity of the effect of corrosion in WTE systems (1). However, in simple terms the fireside corrosion can occur by two major mechanisms. The first mechanism is the weakening of the protective oxide scale on the surface of the tubes. Carbon steel tubes form a protective magnetite scale at the O.D. of the tube. The second mechanism is the dissolution by a molten phase of the scale to expose base metal. The first mechanism leads to spalling where the scale breaks off in localized regions to expose steel to further oxidation. The weakened scale has been linked to the presence of chloride or ferric chloride in the scale. The presence and activity of a molten ash layer on the surface of the heat transfer surface can lead to rapid rates of wall loss and catastrophic failure of tubes. The molten material dissolves the protective scale and the underlying base metal. This process is quite complex and involves a number of issues. These issues include the gas temperature, the metal temperature, the local gas atmosphere (oxidizing or reducing) and the chemical, mineralogical nature of ash. Indeed, without the presence and behavior of the ash corrosion may not proceed at significant rates. It is the characteristics and the mineralogy of the ash and its behavior in the environment (atmosphere and temperature) that will con trol the corrosion process. Therefore, a detailed analysis and characterization of the ash is required in order to understand why and how the corrosion occurs. This knowledge can then be used to develop methods to predict, correct, or control the excessive wastage rates.

This paper will indicate how advanced analytical techniques have been applied to the understanding of deposit formation and fireside corrosion in WTE systems. In particular, methods which have been recently developed and applied to study ash formation and deposition in coal fired systems will be discussed and their usefulness to corrosion issues in WTE systems illustrated. The need to use advanced analytical techniques is based on the experience that the bulk methodologies used to examine ash systems do not provide sufficient insight into the complex processes involved in deposition and subsequent corrosion. These bulk techniques include chemical composition of the ash and powdery-ray diffraction analysis of the ashes and deposits. Chemical analysis provides information on the relative amounts of selected elements (however, usually expressed as oxides) in the sample. Key species such as chlorine, sulfur, lead, etc., can be identified and their potential for corrosion inferred. Extensive study and comparison of chemical composition data is required in order to obtain an understanding of the various reaction and interactions between the fuel-derived species in the furnace. X-ray diffraction analysis provides useful data on the crystalline species present in a sample. While this technique is, at best, semi-quantitative data on the crystalline species in a deposit or ash can be used to establish important processes that have occurred within the deposit and occasionally be used to identify corrosion products. However, as it is a bulk technique where the sample is ground and mixed important data on the species present at or near the corrosion interface can only be inferred from the data. Furthermore, as x-ray diffraction identifies crystalline species only (indeed only those in concentrations greater than 5 wt.) little information is obtained on any amorphous (non-crystalline) phases which may have had a contribution to the corrosion process on the tube surface. A key aspect of corrosion is the rate at which the corrosion products are removed form the interface. A corroding phase with significant amounts of fluid amorphous material will facilitate the diffusion rates of corrosion products. Therefore, techniques are required which can give insight into how and why the deposits form and how these deposits can react with the heat transfer surface and cause wastage. In particular, information on the formation of low melting phases (eutectic compositions) in the furnace and in deposits is required. Furthermore, identification of the speciation of key elements in the ashes and deposits formed in the systems is needed. These key elements include chlorine and sulfur as they have been linked to corrosion processes in WTE. However, while the presence of these elements can be established using bulk chemical analysis techniques data is not readily available in the forms which sulfur and chlorine are present.

The two techniques which can provide this information are computer controlled scanning electron microscopy (CCSEM) and scanning electron microscopy point count (SEMPC). As indicated in the names both techniques are based on scanning electron microscopy (SEM). While SEM techniques, combined with microprobe analysis, have been used for years to study the morphology and chemical interaction at corrosion interfaces the methods tend to be subjective in nature. The microscopist determines the area of interest and the particular features to analyze with microprobe techniques. While this has given some very useful information key aspects can be missed and it is very difficult to relate the characteristics of the ash (dispersion of microscopic particles) to the dense thick deposits and the corrosion interface. Thus, a mechanistic model of the corrosion process can not be readily obtained unless objective, statistically valid data is obtained from the various samples including ash, deposits, and corrosion interfaces.

DESCRIPTION OF SEMPC AND CCSEM TECHNIQUES

The following is a description of two techniques which have been developed recently (2,3) . These techniques have been developed and used extensively for the study and analysis of ash formation, behavior, and deposition, in coal fired systems. The similarities between ashes and deposits from coal fired systems to those of WTE systems allows application of these techniques. Of course, these techniques are used in conjunction and in addition to bulk analysis methods and with conventional microscopic techniques (optical and scanning electron).

Computer Controlled Scanning Electron Microscopy

This technique is used to characterize an ash on a particle by-particle basis. About 3000 particles are analyzed in the method which determines the chemistry (semi-quantitatively), size, shape and area of particles in a given size range (usually 1-100 microns in diameter). Further analysis of the extensive data is obtained by study of the computer output file using a normative program. This program determines whether a given particle fits the chemical composition of one of forty mineral phases common to ash systems. Furthermore, the program can be used to determine the relative amount of the phases analyzed by various parameters such as weight percent as a function of size, volume percent as a function of size and mineralogy, etc. Another important aspect is that the particles which do not appear to fit one of the forty specified phases may be further analyzed by the use of software such as spreadsheets or tailored software. This is especially important in the study of ash systems where particular focus may be on the unclassified particles as they can provide excellent insight into the formation and presence of low-melting phases which can contribute and facilitate the deposition/corrosion process. Examples of output from the CCSEM data includes size distributions on a mineral basis (weight and number percent).

The advantage of the CCSEM technique is that it gives extensive data on the size, shape, and chemistry of particles in an ash. The large number of particles analyzed makes the analysis have statistical relevance to the phenomena of ash behavior. A disadvantage of the analysis is that it can only be applied to ash systems such as fly ash or hopper ash, it has limited application to the study of deposits or corrosion interfaces. Furthermore, the chemical composition data obtained from the CCSEM is somewhat limited and is only sufficient to classify the various particles using a normative routine.

Scanning Electron Microscopy point Count (SEMPC).

The SEMPC technique was developed as a means to objectively analyze ash deposits. In the technique over 200 points are analyzed randomly over a selected area using microprobe analysis technology (thin-window energy dispersive spectrometry). The chemical composition data obtained from each point (3-5 microns in diameter) is then stored on a computer file for subsequent analysis. This analysis involves the classification of the chemical composition in a similar manner to that used for the CCSEM data. However, as the chemical composition data is more rigorous than that obtained from CCSEM data more accurate classifications can be made. The enhanced chemical composition data allows excellent insight into the chemical processes that can occur within a deposit. Features such as molar ratios, viscosities, baselacid ratios can be established. An important aspect with respect to corrosion is the ability to assess the amount of base metal associated within the corrosion or deposit products. This is a complex procedure and involves detailed evaluation of the SEMPC data using a series of specially tailored computer programs.

EXAMPLES OF DATA *Characterization of* ***Deposits and Ashes***

During a recent outage at a WTEfacility burning refuse-derived fuels selected samples were collected. Corrosion of the low temperature superheater had been recorded during recent inspections. The wall thickness of the carbon steel tubes had been reduced from the original 0. 160" minimum ordered wall to approximately 0.050" during the six years of service. However. based on ultrasonic thickness survey results significant wastage was determined to have occurred in the sixth year of service. The samples collected included deposits from the slag screen, boiler bank or generating bank, low temperature superheater and high temperature superheater. Two ashes were also collected. These included an ash from the economizer hopper and loose ash from the cavity below the generating bank. The samples were subjected to a detailed characterization and evaluation to determine the deposition and corrosionlerosion potential. The analysis included x-ray diffraction of all deposits and ashes and detailed morphological and chemical analysis using scanning electron microscopy with electron microprobe analysis. The latter technique involved microprobe analysis of selected features and multi-element mapping. The ash deposits and the loose boiler bank ash were further analyzed by SEMPC. The economizer ash and loose boiler bank ashes were characterized by CCSEM analysis.

Table 1 lists the results of x-ray diffraction analysis of the economizer ash and the low temperature superheater. The results show that there were significant differences in the crystalline phase assemblage between the two samples. The deposit from the low temperature superheater contained calcium sulfate (anhydrite), lead sulfate, lead silicate as major phases with minor phases of quartz and lead oxide. The economizer ash sample contained a major phase of quartz with minor amounts of calcium sulfate, iron oxide, calcium carbonate, sodium sulfate, and a calcium aluminosilicate (plagioclase phase such as anorthite). These results show that there are major phase differences between the ash and the deposits. All the crystalline phases observed in the ash can be assumed to have been directly derived from the fuel source with no real evidence of interaction or reaction during the combustion process with other ash particles. The low temperature superheater deposit was ore complex in phase assemblage. Indeed, the phase assemblage is dominated by the lead phases. All three lead crystalline phases observed would not be expected to promote corrosion. The lead oxide, sulfate, and silicate would be stable at elevated temperatures and would have low diffusion coefficients through the deposit to the tube surface. There was no evidence of a chloride or reduced phase of lead. Of further interest in the x-ray diffraction is the absence of phases containing the other elements known to be present in the samples. These elements must be either in the amorphous phase or within crystalline phases which are not in sufficient quantities to be detected by x-ray diffraction.

TABLE 1 X—Ray Diffraction Results Economizer Ash and LTSH Deposit

Economizer Ash	
Major Phase	.... Quartz
Minor Phases	.... Calcium Sulfate
	.... Iron Oxide
	.... Calcium Carbonate
	.... Plagioclase
	.... Sodium Sulfate
LTSH Ash	
Major Phases	.... Calcium Sulfate
	.... Lead Sulfate
	.... Lead Silicate
Minor Phases	.... Quartz
	.... Lead Oxide

In order to indicate the wealth of data obtained by CCSEM and SEMPC an their application to corrosion potential of ash examples of the data will be given. Table 2 lists the phase assemblage of a WTE ash taken from the economizer and the boiler bank. The analysis shows the complexity of the phase assemblage. Not only are there a large number of phases present but there are also marked differences between the ash collected in a region associated with the boiler bank and the ash which has passed through the unit (economizer). There is also a marked difference in the phase assemblage of the boiler bank ash with respect to that reported from the x-ray diffraction analysis. It should be noted that the unclassified phases for both samples did not contain lead or zinc in a measurable quantity. The unclassified were predominantly calcium rich with some sulfur associated with them. Furthermore, analysis of the unclassified particles in the economizer sample showed that chlorine was associated with the calcium rich grains. A significant difference between the WTE ashes and the ashes from coal-fired boilers is the low levels of iron phases in the WTE ashes. The two samples analyzed only had less than 0.5 volume % of iron oxide particles. Coal ashes usually contain above 5 volume % iron rich particles (dependent on source). An important aspect also is the level of quartz and clay species (kaolinite, montmorillonite and illite in the ashes). Quartz is important as it can cause erosion of tube surfaces. While the level of the quartz was about the same for the two samples, further analysis of the CCSEM data showed that the quartz in the boiler bank ash sample was much coarser than the quartz in the economizer ash. The presence of clay species (kaolinite, montmorillonite, and illite) is probably due to the contamination of the fuel with soil or dirt. These phases are important as they can contribute to the mass and density of deposits. The illite, for example contains potassium which can lead to low melting silicate phases and possibly a fluid corrosive phase.

Table 2 Phase Assemblage of Ash Samples - CCSEM Data

Phase	Economizer Ash	Boiler Bank
QUARTZ	4.4	5.2
IRON OXIDE	0.3	0.4
FUTILE	0.4	0.3
ALUMINA	0.1	1.1
CALCIUM OXIDE	0.2	4.5
DOLOMITE	0.2	0.9
KAOLINITE	5.6	11.1
MONTMORILLONITE	0.2	0.7
K ALUMINOSILICATE	1.5	2.1
CA ALUMINOSILICATE	4.7	7.0
NA ALUMINOSILICATE	3.2	3.7
ALUMINOSILICATE	0.9	2.5
MIXED ALUMINOSILICATES	2.8	4.3
CALCIUM SILICATE	1.9	1.6
CALCIUM ALUMINATE	0.2	0.0
GYPSUM/ANHYDRITE	10.2	1.6
APATITE	0.8	0.4
POTASSIUM CHLORIDE	0.3	0.0
GYPSUM/BARITE	0.3	0.0
GYPSUM/ALUMINOSILICATE	6.2	2.8
SILICA-RICH	3.6	6.9
CALCIUM OXIDE-RICH	0.9	5.5
CALCIUM OXIDE AND SILICA RICH	0.8	1.1
UNCLASSIFIEDS	50.4	34.3

The phase assemblages of the deposit samples as determined by SEMPC analysis are listed in Table 3. It is not prudent to discuss the mineralogy and origin of all the phases detected. However, of importance is the differences in phase assemblage of the various deposits going through the system and the influence of these deposits on the corrosion process. The predominant phase in all the samples is calcium sulfate. The boiler bank deposit, however, was predominantly unclassified with only 4 % as calcium sulfate. The superheater samples and the boiler bank deposit contained significant unclassified points. These points were assumed to be amorphous (non-crystalline). Detailed investigation of the unclassified points showed that for these samples the points were rich in calcium and sulfur with some lead associated in the sulfate matrix. There was only limited amounts of chloride observed in the unclassified phases. The unclassified points of the boiler bank and slag screen deposits were rich in alulninosilicate phases.

TABLE 3 PHASE ASSEMBLAGE OF DEPOSIT SAMPLES-SEMPC DATA

PHASE	**SLAG SCREEN**	**BOILER BANK**	**LTSH**	**HTSH**
ANORTH11B	0.4	0.0	0.0	0.0
ALB1'1E	2.0	0.0	0.0	0.0
LEUCITE	1.2	0.0	0.0	0.0
QUARTZ	2.8	0.8	1.2	0.8
CALCIUM OXIDE	0.8	0.0	0.0	0.0
ALUMINUM OXIDE	0.4	0.0	0.0	0.0
ANHYDRITE	47.8	4.0	30.9	19.6
SODIUM CALCIUM SULFATE	2.8	7.6	3.2	3.2
KAOLINITE	0.8	0.4	0.4	0.0
ILLITE	1.2	0.4	0.8	0.4
MONTMORILLONITE	0.0	0.0	0.8	0.0
UNCLASSIFIED	39.8	86.4	62.6	76.0

Other data obtained from SEMPC analysis is the determination of the chemical composition of the sample (obtained by averaging all the points analyzed). The chemical composition date of the deposit samples are listed in Table 4. The results show that there was an increase in lead content with metal temperature (going from the slag screen tube deposit to the high temperature superheater). This contrasts with the reduction in relative levels of silica and alumina in this progression. The boiler bank deposit was very rich in sodium and potassium compared to the other samples. All the samples contained less than I wt% chlorine. This level of chlorine is not considered to be excessive. There was no zinc detected in the samples. The results show the complexity of the chemical composition of ash deposits.

TABLE 4 CHEMICAL COMPOSITION OF DEPOSIT SAMPLES (SEMPC DATA)

OXIDE COMPONENT	**SLAG SCREEN**	**BOILER BANK**	**LTSH**	**HTSH**
SIO2	17.4	9.1	8.9	7.9
AL203	9.5	6.1	4.9	5.6
FE203	1.2	0.7	1.1	1.0
TIO2	0.9	1.1	0.6	0.9
P205	0.9	0.6	0.9	0.4
CAO	9.0	7.2	14.1	8.2
MGO	1.1	1.2	1.1	1.2
NA2O	4.9	10.1	3.7	3.8
K20	3.5	9.3	4.1	4.6
S03	37.9	33.7	30.5	23.1
BAO	0.1	0.1	0.1	0.1
CR203	0.2	0.1	0.1	0.1
CLO	0.2	0.8	0.2	0.1
PBO	0.4	20.1	29.5	43.0

DISCUSSION

Significant research on the fireside corrosion of heat transfer surfaces in boilers has indicated the importance of elements such as chlorine, sulfur, zinc, and vanadium. As part of the process to understand the corrosion mechanisms in WTE systems these elements and their mode of occurrence or transport properties must be established. The vanadium is usually associated with oil-fired systems and is not considered a significant component in municipal solid waste or relevant to corrosion processes. However, an important element in ash which could be related to corrosion is that of lead. This element is also important in terms of environmental issues.

SEMPC and CCSEM analyses were used to determine the association of sulfur, lead and chlorine in the ash samples and the deposits. The results showed that the lead in the deposits was distributed throughout the sample including the matrix. In many areas the lead was with the sulfate matrix (an admixture of calcium, sodium, and potassium sulfate). This type of matrix would be expected to melt at low temperatures (1) and contribute to diffusion of the scale material. Some lead was present as discreet inclusions as evidenced by the detailed microprobe analysis and examination of the sample morphology, see Figure 1. There was little evidence of chlorine or zinc in the deposits and ashes.

The analysis of the CCSEM data for the economizer and boiler bank ashes shows a clear association of chlorine with calcium in the unclassified phases. Indeed, while the CCSEM chemical analysis does not provide rigorous chemical composition the determination of the Ca/Cl molar ratio distribution for the ash shows that the bulk of the points identified as rich in calcium and chlorine for the economizer ash had a molar ratio of about 1:2 corresponding to calcium chloride. It should also be mentioned that these calcium/chlorine rich particles were relatively pure with little or no evidence of other elements. Figure 1 shows the Ca/Cl molar ratio for the two ash samples as a function of size. The graph shows that the "calcium chloride" particles are present in the size range between 1 and 50 microns. Furthermore, the bulk of the calcium chloride particles are below 5 microns. The identification of the calcium chloride phase is important as calcium chloride can lead to corrosion at low temperatures such as during shutdown. Furthermore, when deposited on the surface of the tubes in the furnace and the convective pass the calcium chloride would tend to dissociate and then react with the sulfur in the flue gas and release chlorine within *the* deposit which can *then* migrate to the steel *surface*. Indeed, it should be noted that there was limited amounts of calcium sulfate in the economizer ash. This would lead to the assumption that the calcium is transported as a chloride and then the chloride would react or dissociate to form the more stable sulfate. Certainly, the results of the ash analysis shows that there is very little sulfur associated with the particles. This contrasts to the results of the SEMPC analysis of the deposits which shows significant levels of sulfur present (usually in the form of a sulfate such as anhydrite or mixed sulfate). Furthermore, the chloride levels in the deposits are very low. There was no evidence to suggest a zinc chloride phase was present based on the chlorine levels and the absence of a definitive zinc peak in the energy dispersive spectrum. More research is required to characterize the ash deposits and scales using SEMPC techniques in order to develop a model of interaction between the ash species and the heat transfer surfaces.

CONCLUSION

Techniques have been described which provides valuable insight into the role of ash components in WTE systems with respect to fireside corrosion. An important observation is the occurrence and fate of chlorine associated with the ash. The CCSEM analysis showed that for the economizer a significant quantity of particles were considered to be predominantly calcium chloride over the size range 0-50 microns. Comparison of this result with the ash from the boiler bank showed that there were few calcium chloride particles present. Indeed, the calcium particles appeared to be rich in sulfate. This data combined with the low concentration of chlorine in the deposits and the predominantly calcium-rich sulfate matrix suggests that the transport of calcium to the deposit is via calcium chloride. This process can lead to chlorine reacting with the scale and cause spalling or corrosion. The high levels of lead in the deposits from the boiler bank, and the superheater surfaces and the absence of lead species in the economizer ash indicates that the lead is preferentially deposited on heat transfer surfaces. This can be understood if one considers a particle impaction model for deposition where the dense material will have a greater tendency to stick to a target surface irrespective of the nature of the target.

Through the detailed examination of the characteristics of the ashes and deposits on heat transfer surfaces in the boiler methods to reduce or mitigate the corrosion processes can be developed. Application of the described techniques will involve the examination of further ashes and deposits coupled with corroded samples from WTE facilities. The techniques described in this paper give a framework with which to formulate corrosion mechanisms for boiler designers and engineers. It is hoped that through a detailed applied program of the investigation of the interaction of the ash components with the steel surfaces methods to mitigate the corrosion process can be developed. This will result in longer life of heat transfer surfaces, shields, and a major reduction of forced outages. Mitigation techniques may include the tighter control of material in the feed stock, increased use of boundary air at side walls, control of fireball, better coatings or cladding at fireside surfaces. The adoption and application of the characterization methods described herein will allow the accurate assessment of the effects of these mitigation methods.

A further aspect of this research is the ability to model the deposition behavior of the ash. This modeling can then be used to assess sootblowerlocation and operation in WTE systems. In many instances the sootblowers remove deposits which are passive and do not contribute to corrosion of the scale and the base metal of the tube. However, the removal of the deposit by a sootblower can expose bare metal to the corrosive environment and accelerate wastage of the tube.

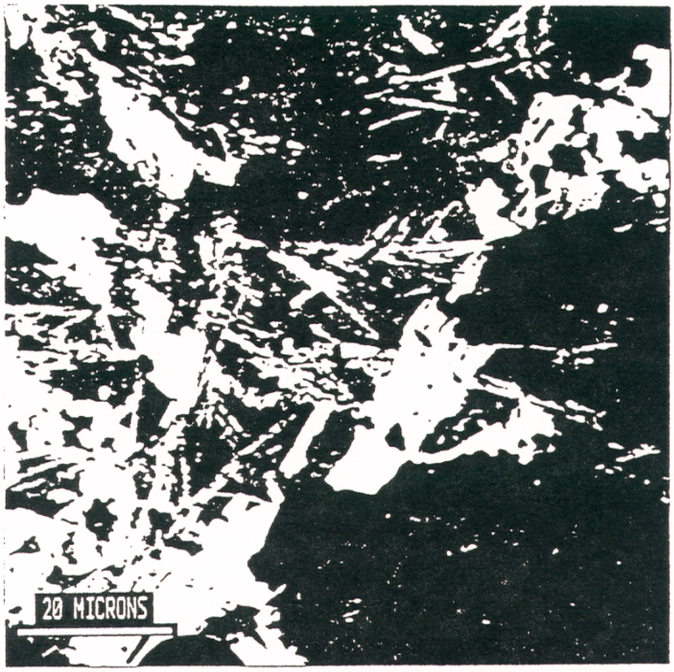

Figure 1. Scanning electron image of cross-section of TTSH deposit showing the complex phase assemblage. The bright regions/crystals are rich in lead and the matrix is rich in calcium sulfate.

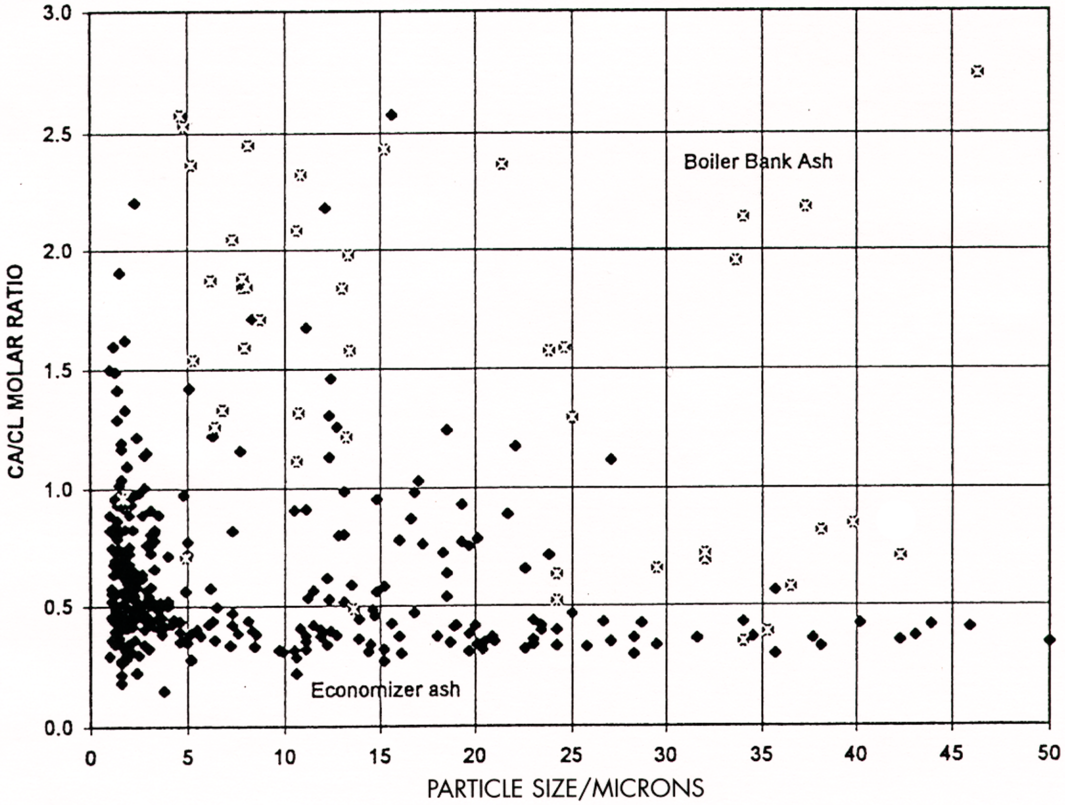

Figure 2. Plot of Ca/Cl molar ratio for calcium rich particles detected and analyzed by CCSEM analysis.

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