



Mineralogical investigations into clinker formation and variations in deposit characteristics with time in a large-scale pc-fired boiler



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HIGHLIGHTS

- Mineralogical analysis of deposits show reasons behind its variation with time.
- Phase equilibrium data suggests clinker formation at high temperatures.
- Optical microscopy shows crystalline nature of clinker deposits.
- Occurrence reaction rims on quartz grains in new clinker deposits.
- Phase equilibrium diagram revealed crystallization temperatures of clinkers.

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ABSTRACT

Clinker deposit samples were provided by a power utility company in order to determine the conditions of formation and the nature of the variation in the deposits as a function of time. The samples collected from the utility (two sets of new clinker deposits and one old clinker deposit) were examined using a combination of bulk chemical analysis to determine the major element chemistry, mineralogy by quantitative X-ray diffraction and optical microscopy. The chemistries of the old clinker sample and new clinker sample were found to be similar, suggesting that variations in boiler operating conditions, rather than variation in ash chemistry of the feed coal, is largely responsible for the change in clinker characteristics with time. These observations are also well supported by the distinctive mineralogy of old and new samples, in spite of the similarity in bulk chemistry. The mineralogy of both samples of the new clinker also suggests formation at a higher temperature than the sample of the old clinker and possibly under more reducing conditions in the case of another set of samples.

Optical microscopy indicates that the thicker pore walls and more crystalline nature of the new clinker deposit samples in comparison to the old clinker deposit are most likely responsible for the greater strength of the former. The deposit textures as observed in the optical microscopy support the higher temperature of formation of the new deposit samples as shown by the occurrence of the reaction rims on many of the quartz grains and the complete resorption of fly ash particles. Additionally, the application of phase equilibrium data using the $\text{SiO}_2\text{-FeO-Al}_2\text{O}_3$ system also supports the hypothesis that the new clinker deposit has formed at higher temperature, indicating initial temperatures of crystallization of 1500 °C and 1475 °C for new clinker deposits and 1450 °C for the old clinker.

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1. Introduction

Pulverised coal combustion has been and continues to be one of the main conventional methods of producing electricity. Mineral matter present in coal may occur as free ions, salts, organically associated inorganic elements and crystalline minerals. During

coal combustion this mineral matter may partly vapourise, fragment or coalesce. The mineral matter in coal transforms into ash during combustion which may result in ash deposition, causing problems such as fouling and slagging. Slagging deposits forming in the radiation zone directly exposed to the flame radiation are generally called clinkers whereas sintered deposits formed in the convection zone not directly exposed by flame radiation are referred to as fouling deposits [1–6]. Clinkers have been a recurring problem in all coal-fired boilers for as long as humans have operated coal boilers.

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Coal clinkers form when the inorganic elements contained in coal such as iron, calcium, silicon, aluminium and sodium interact with sulphur and carbon at high temperatures. These reactions may lead to the formation of a glassy slag that eventually hardens into clinker. Clinker formation is a complex series of mineralogical transformations and phase changes that occur as coal burns. Small clinkers can fuse together to form large ones that can physically damage boilers.

The troublesome formation of clinkers in the furnace and the formation and growth of clinkers on furnace linings requires special consideration in power utilities. If the clinkers are allowed to form on boiler surfaces, it could eventually drop off from upper sections of the furnace and damage the lower sections of boiler (for eg. hopper tubes at the bottom of the boiler). This is expected to result in a forced shut down of the unit and requires maintenance. In majority of these cases, this trouble can be either greatly reduced or avoided, as clinkers are formed by the fusion of ash which remains after the combustion of coal in the furnace. Clinker formation in boilers is largely governed by the coal quality as well as the combustion conditions in the boiler. In an effort to understand the origin of clinker formation, systematic study into the elemental analysis and mineralogy of coals and clinkers is essential. Since there is no systematic mineralogical analysis pertinent to clinker formation in boilers in the open literature except for experimental and modelling based studies on ash deposition [6–15] and identification of clinker formation [16], an attempt has been to deduce the reasons behind clinker formation and changes in deposit characteristics with time in a 330 MW large scale power utility boiler located in Western Australia. Typically, previous studies of clinker formation have used an approach based upon chemistry. In this paper, classical mineralogical techniques as used by petrologists in the study of metamorphic and igneous rocks which have formed under similar high temperature conditions have been applied to the study of clinker formation. This approach makes use of the wealth of information that has been gathered over many decades of study of natural systems and its application to deposit formation in pf boilers. The studies have been carried out with the aim of understanding the combustion conditions that could have possibly led to the formation of these sintered deposits on boiler surfaces. This analysis also helps in predicting the temperatures at which the bulk of clinker would have started to form. Based on the analytical results, the paper summarises the reasons for clinker formation and predicts the likely temperatures of clinker formation based upon mineralogical phase relations.

2. Sampling and analytical procedures

Three samples of boiler deposits were submitted for analysis (see Table 1). The “old” and “new” clinker deposits are separated by a period of several months of boiler operation with a consistent feed coal composition and feed particle size. Proximate and ultimate analyses of subbituminous feed coal are presented in Table 2. Although no information on the size of the three deposit samples are provided by the utility personnel, it should be noted that the size of these deposit fragments from our visual observations at the time of investigation ranged from 150 to 200 mm. Sub-samples

Table 1
Details of ash deposit samples submitted for analysis.

Sample Id.	Sample description
A	Old, friable clinker (labelled as old clinker)
B	Massive hard, grey clinker (labelled as new clinker sample 1)
C	Vesicular grey clinker (labelled as new clinker sample 2)

Table 2
Proximate and ultimate analyses of sub-bituminous coal^a (as received basis in wt%).

	Range	Average
<i>Proximate analysis (%db^b)</i>		
Moisture	22–31	25.0
Ash	4–10	8.0
Fixed Carbon	22–34	29.8
Volatiles	36–48	37.7
<i>Ultimate analysis (%daf^c)</i>		
Carbon	73–76	73.5
Hydrogen	4.2–4.9	4.8
Nitrogen	1.2–1.5	1.2
Sulphur	0.3–1.3	1.0
Oxygen	18–20	19.5
Specific Energy(MJ/kg)	18.8–21.5	19.6
<i>Ash analysis (% db^b)</i>		
SiO ₂	47–59	51.4
Al ₂ O ₃	31–36	33.5
Fe ₂ O ₃	5–10	7.4
CaO	0.4–2.1	1.8
MgO	0.2–1.1	0.86
Na ₂ O	0.02–0.3	0.24
K ₂ O	0.2–0.4	0.33
TiO ₂	0.4–2.0	0.99
Mn ₃ O ₄	0.06–0.08	0.07
SO ₃	0.06–0.35	0.21
P ₂ O ₃	0.65–2.15	1.60

^a Coal type is from Western Premier Mine, Australia.

^b Dry basis.

^c Dry ash free.

were taken of the deposit samples for X-ray diffraction analysis, bulk chemical analysis and for optical microscopy examination.

The boiler is a pf boiler of a horizontally opposed burner configuration with three rows of burners at the furnace front and 2 rows at the rear (Fig. 1) with each row consisting of 5 burners, each attached to an individual pulveriser. The load varies from 250 MW to 320 MW and the furnace gas temperature varies from 1200 °C to 1300 °C. Typically deposits from as eyebrows on the furnace walls just above the burners (and in the superheater and reheater zones (Fig. 1).

The samples for X-ray diffraction analysis were ground in an agate mortar and pestle then packed into an aluminium holder. All samples were run on a Philips 1050 goniometer operated at 45 kV, 30 mA and using Co K α radiation in conjunction with a graphite monochromator and divergence and receiving slits of 1° and 0.02 mm respectively. All traces were run in step mode at 0.04° step intervals with a 10 s counting time per step over an angular range of 3–90°. Peak identification was performed using Bruker Eva search/match software. Quantitative X-ray diffraction analysis was performed using SIROQUANT™, a quantitative X-ray diffraction analysis software package that uses Rietveld procedures to generate a synthetic pattern which is then matched to the experimental data using a least squares minimisation fitting procedure. This approach has the advantage that the complete diffraction pattern is used to derive the quantitative results rather than relying upon one or two peaks for the determination. Although application of the Rietveld procedure usually requires that the phases be crystalline in order to calculate the synthetic XRD pattern, SIROQUANT makes use of experimentally derived structural data (observed hkl files) for amorphous or poorly crystalline phases and thus can be used to determine the amount of amorphous material present in the sample.

Major element analysis of the deposit samples was carried out using ICP-AES following fusion of the sample with lithium metaborate/tetraborate and dissolution of the fused sample in acid.

The samples were sectioned normal to visible structures, where present. Sample blocks selected for optical microscopy were cut

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