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Estimating the first melting temperature of fireside deposits in recovery boilers

Scope

The first melting temperature (FMT) of fireside deposits is important in recovery boiler operation. Corrosion of superheater tubes occurs rapidly if tube surface temperatures exceed the FMT of the deposits on the tubes. In addition, for recovery boilers burning liquor with high chloride (>2.5 wt% Cl on dry black liquor solids), deposits contain a large amount of liquid phase when they melt. In such a case, the FMT is also the temperature at which deposits become sticky, and deposit accumulation accelerates.

This TIP summarizes available information on the effects of deposit composition on FMT, and shows how to estimate the FMT based on deposit composition.

Definitions

The First Melting Temperature (FMT) is the minimum temperature at which some liquid phase is present in a multi-component mixture. For recovery boiler deposits, the FMT is the temperature at which deposits begin to melt.

Materials

Not applicable.

Safety precautions

Not applicable.

Introduction

Fireside deposits in kraft recovery boilers melt gradually over a range of temperature. This behavior is important for both boiler design and operation. The first melting temperature (FMT), the temperature at which the deposit begins to melt, is particularly important in superheater corrosion. Field studies and mill experience show that accelerated corrosion of superheater tubes occurs if the tube surface temperature exceeds the FMT of the deposit that covers the tube surface (1-4), particularly when the atmosphere around the tube is reducing. The FMT is also important in boilers that burn high chloride black liquor (>2.5 wt% Cl on dry solids or >8 mole% Cl/(Na+K)). At such high chloride levels, the FMT is also the temperature at which the deposit becomes sticky so that massive deposit accumulation can occur (5).

Deposits consist mainly of sodium sulfate (Na_2SO_4) and sodium carbonate (Na_2CO_3), and small amounts of sodium sulfide (Na_2S), sodium chloride (NaCl) and analogous potassium (K) salts. The FMT typically varies between 520 and 580°C (970 and 1075°F), depending on composition. In recent years, trends toward mill closure, increased use of hardwoods, and high solids firing in recovery boilers have led to increased chloride, potassium, and carbonate contents in recovery boiler deposits and precipitator dust. Such changes in deposit composition are expected to have a significant effect on the deposit melting behavior.

This TIP summarizes available information on the effect of composition on the FMT, and shows how to estimate the FMT from deposit composition. It is based mainly on the *TAPPI Journal* paper of Tran, Gonsko and

Mao (6). The paper includes a discussion of the theory of the phase behavior of ionic melts, which is essential to a full understanding of how different deposit components affect melting. Interested readers are referred to the paper for details.

FMT vs. composition of deposits

The FMT is a consequence of the behavior of multicomponent ionic melts. The ionic species that make up recovery boiler fireside deposits are the cations sodium (Na^+) and potassium (K^+), and the anions carbonate (CO_3^{2-}), sulfate (SO_4^{2-}), sulfide (S^{2-}) and chloride (Cl^-). Components that form solid solutions with each other tend to have an effect on FMT, while those that tend to form eutectics have little or no effect. Of the species present in recovery boiler deposits, only potassium (K^+) and carbonate (CO_3^{2-}) would be expected to appreciably affect the FMT.

Measurements of the FMT and composition of over 150 deposit and precipitator dust samples confirmed that FMT decreased as potassium content increased [6]. However, the data on the effects of carbonate (as well as chloride) showed a great deal of scatter, partly because of variations in potassium levels. In order to isolate the effect of individual components, a systematic study was carried out using synthetic deposits.

The data in this TIP were obtained from this systematic study. The deposit samples were prepared by mixing pure chemicals to give the desired compositions, melting the mixture at 800 to 900°C (1470 to 1650°F) for 20 minutes, cooling the melt and grinding the frozen melt. The FMT was determined by Differential Thermal Analysis (DTA). Figure 1 shows the effect of carbonate on the FMT of deposits which contain 5 mole% $\text{Cl}/(\text{K}+\text{Na})$ and different K contents. At K contents below 7.5 mole% $\text{K}/(\text{K}+\text{Na})$, increasing the carbonate content, up to about 50 mole % $\text{CO}_3/(\text{Na}_2+\text{K}_2)$, decreases the FMT. A further increase in carbonate results in a higher FMT, which is consistent with the minimum melting behavior of a carbonate-sulfate mixture. At K levels above 7.5 mole % $\text{K}/(\text{Na}+\text{K})$, the effect of carbonate on FMT is only present at lower carbonate contents. At the highest potassium levels, >15-20 mole% $\text{K}/(\text{K}+\text{Na})$, the effect of carbonate becomes minimal.

Figure 2 shows the effect of carbonate on the FMT of deposits containing 5 mole% $\text{K}/(\text{Na}+\text{K})$, for two different chloride levels: 5 and 10 mole% $\text{Cl}/(\text{Na}+\text{K})$. No significant difference was found between these two chloride levels, confirming the insignificant effect of chloride on the FMT.

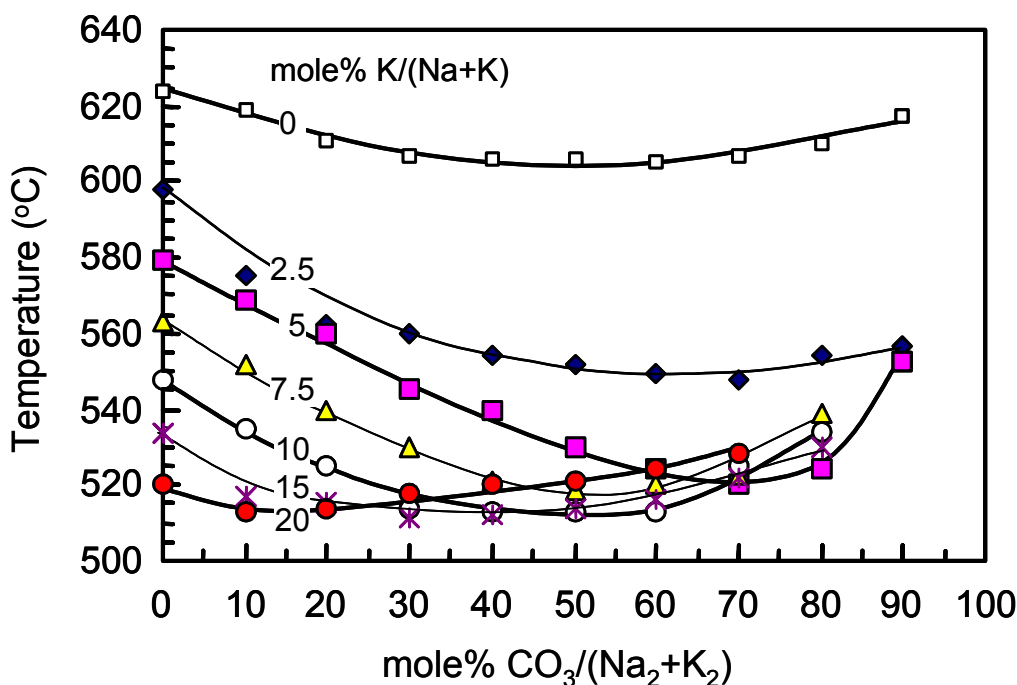


Fig. 1. Effect of Carbonate on the FMT of Synthetic Deposits at Different Potassium Levels (5mole% $\text{Cl}/(\text{Na}+\text{K})$).