Modeling fine particles and alkali metal compound behavior in a kraft recovery boiler

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ABSTRACT: Under certain conditions, ash in black liquor forms a locally corrosive environment in a kraft recovery boiler. The ash also might cause efficiency losses and even boiler shutdown because of plugging of the flue gas passages. The most troublesome compounds in a fuel such as black liquor are potassium and chlorine because they change the melting behavior of the ash. Fouling and corrosion of the kraft recovery boiler have been researched extensively, but few computational models have been developed to deal with the subject. This report describes a computational fluid dynamics-based method for modeling the reactions between alkali metal compounds and for the formation of fine fume particles in a kraft recovery boiler furnace. The modeling method is developed from ANSYS/FLUENT software and its Fine Particle Model extension. We used the method to examine gaseous alkali metal compound and fine fume particle distributions in a kraft recovery boiler furnace. The effect of temperature and the boiler design on these variables, for example, can be predicted with the model. We also present some preliminary results obtained with the model. When the model is developed further, it can be extended to the superheater area of the kraft recovery boiler. This will give new insight into the variables that increase or decrease fouling and corrosion

Application: The modeling method presented in this article can help boiler designers to better understand how the local conditions affect the alkali metal chemistry and fine particle formation in a kraft recovery boiler, and it can be used to predict corrosion and fouling tendencies under differing operational conditions.

Black liquor is used to fuel kraft recovery boilers, but because of its composition, black liquor is difficult to combust. Black liquor has a high ash content, which is approximately 40% of the dry matter. Vaporization of the ash-forming compounds (i.e., sodium [Na], potassium [K], sulfur [S], and chlorine [Cl]) is an unwanted side effect of the necessary reactions in a kraft recovery boiler [1]. Chlorine and potassium, in particular, have a significant effect on the fouling and corrosion behavior of kraft recovery boilers because they decrease the first melting temperatures of particles and deposits, and increase the amount of liquid phase in them at temperatures above the first melting temperature. As a consequence, steam temperatures and pressures in the kraft recovery boiler have to be constrained to relatively low values in comparison with those used in power boilers [2]. Typical values for maximum steam temperature and pressure in a kraft recovery boiler are 480°C and 85 bars.

In their gaseous forms, alkali chlorides (sodium chloride and potassium chloride) are harmful when they condense on the boiler surfaces because they can react with the tube material in the boiler walls [3]. In addition to this gas phase corrosion, potassium and chlorine can cause molten phase corrosion, which occurs when completely or partially molten fume particles stick to the tube surface [4]. Chlorine and potassium affect the melting range of the particle deposits in different ways: potassium lowers the first melting temperature of a deposit, whereas chlorine increases the amount of liquid phase in the deposit at temperatures above the first melting temperature [5]. Therefore, the chlorine content of the ash particles has a more significant effect on the sticky temperature of the deposit. Even a very small amount of chlorine significantly increases the corrosiveness of the deposit at temperatures above its melting point [6].

Mikkanen [7] and Pyykönen [8] have studied aerosols in kraft recovery boilers. Their works concentrated on aerosol measurements and the modeling of aerosol behavior. However, the modeling method we present differs from previous work because it simulates the aerosols in three dimensions with the Fine Particle Model (FPM) software. FPM can be used to model the particles in a Eulerian reference frame, which means that the modeling framework remains fixed in space, and conservation equations for the amount of each chemical species in each fixed computational cell can be calculated. To our knowledge, this kind of modeling of the alkali metal compounds in a kraft recovery boiler has not been done before. The main objective of the modeling presented here is to predict the local corrosion conditions in a kraft recovery boiler furnace and its superheater area. This can be done by modeling the chemical reactions of the alkali metal compounds and solving the conservation equations for them in the boiler concurrently with a computational fluid dynamics (CFD) simula-

tion. The effects of different operating conditions and parameters on these variables also can be examined.

In this report, we focus on describing the modeling of fume particles that form as a result of the condensation of gaseous alkali metal compounds. The model focuses on the behavior of sodium and potassium chloride. These alkali chlorides turn into particles, mainly through condensation [9], and form a significant part of the fine fume particles. We did not model the entrained liquor droplets that form carryover particles. This is because the carryover particles are significantly larger than the fume particles, and their behavior is governed by entirely different physical phenomena, such as flue gas velocity and gravity. Furthermore, the corrosion phenomena of the carryover particles result from a local reducing atmosphere and molten sulfide compounds [4], whereas the corrosiveness of the fume particles is based on chlorine and potassium. The carryover particles contain hardly any chlorine, whereas the mass of the fume particles contains 1%–2% of chlorine [10].

The principle of the modeling method and some earlier results have been presented in previous publications by the same research team [11,12]. These publications, however, did not include the modeling of potassium compounds, which is presented here.

MODELING PROGRAMS

The modeling method we present is based on three different types of computer software: CFD-based ANSYS/FLUENT [13], the Fine Particle Model (FPM) [14], and the chemical database FactSage [15]. The modeling itself is three dimensional and steady state.

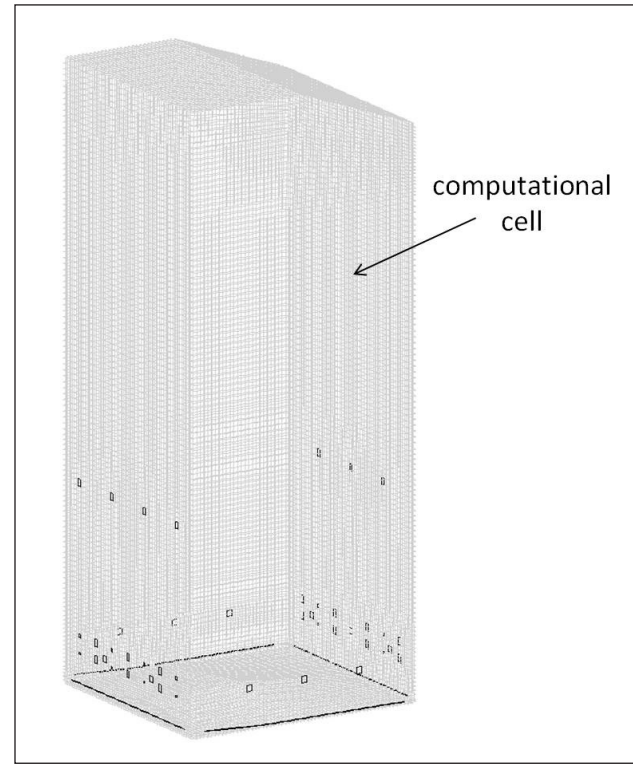
ANSYS/FLUENT is commercial software used to model fluid flow, heat transfer, and black liquor combustion. FPM is a particle dynamics program that is coupled with ANSYS/FLUENT. It simulates the formation and interaction of particles in an Eulerian reference frame by concentrating on the particle populations, the size distribution of which is presented with a probability density function. Above all, FPM is used to model the particles formed from the condensable gaseous species in different chemical reactors. Therefore, it can be used to model the fine fume particle formation in a kraft recovery boiler as well. The characteristic applications of FPM are the simulation of particle formation, growth, and deposition, and it has been used in earlier studies, especially for atmospheric aerosol modeling [16].

In addition to ANSYS/FLUENT and FPM, other computational tools have been used for aerosol modeling. The modeling of chemical reactions requires tools that contain information about different chemical compounds and reactions. Saw et al. [17], for example, have used FactSage for studying the reactions of atomic sodium in black liquor combustion. With FactSage, it is possible to model all of the gaseous, liquid, and solid species of the Na-K-Cl-S-oxygen (O)-carbon (C)-hydrogen (H)-nitrogen (N) system and to calculate what species are present in the reaction equilibrium. Saw et al. [17] make the assumption that the residence time of the flue gas in the kraft recovery boiler is long enough for reaching equilibrium, and therefore the kinetic factors of the chemical reactions do not have to be considered. Jokiniemi et al. [9] share the same view.

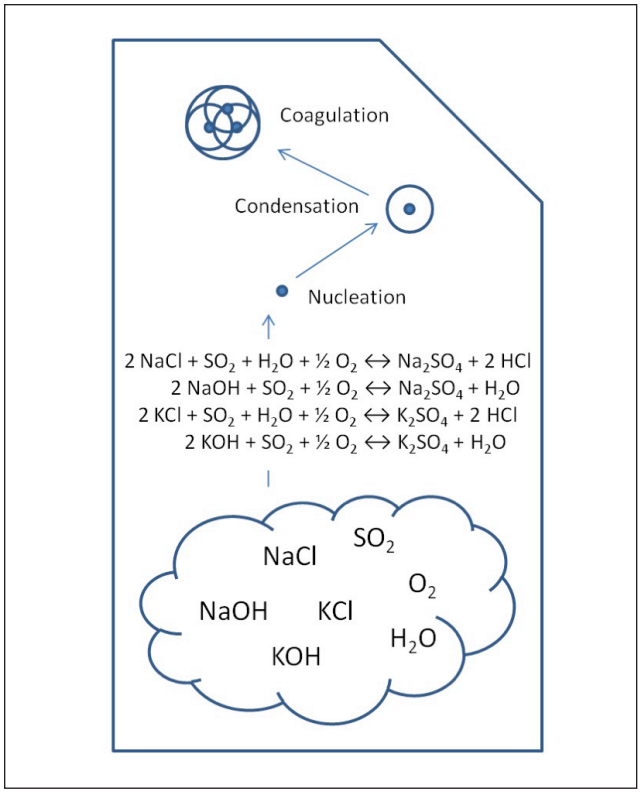
MODELING METHOD

As the sample for our model, we used a medium-sized recovery boiler with a black liquor capacity of 4000 tons of dry solids per day. The black liquor burned in this boiler contains 0.6% chlorine and 4.0% potassium in the dry solids. **Figure 1** shows the computational grid of the boiler furnace. The computational grid of the boiler furnace is comprised of around 400,000 cells, and at this point the modeling focuses solely on the boiler furnace below the nose arch. In the simulation, the conservation equations for mass, momentum, and energy are solved numerically. These equations are based on the Reynolds-averaged Navier-Stokes equations, and the realizable k-epsilon model is used for turbulence modeling.

The modeling method we present is a simplification of the various processes taking place in a kraft recovery boiler. For now, the model only examines what is happening in the boiler furnace below the nose arch. Because the superheater area is not taken into account yet, the deposition of the particles is not modeled. Another simplification in the model is that sodium and potassium carbonates are not yet taken into consideration. As a consequence, only alkali sulfates (sodium sulfate, potassium sulfate) and alkali chlorides (sodium chloride, potassium chloride) are assumed to condense onto the fine fume particles. Furthermore, because sodium sulfate is considered



1. Computational grid.



2. The modeling method.

the main compound in the fine fume particles [7,8], and alkali sulfates are the first alkali species to condense in the kraft recovery boiler furnace [18], sodium sulfate is assumed to be the only compound that forms new particle seeds through nucleation.

Figure 2 depicts the principle of the modeling method. The figure is a simplified scheme, because in the actual modeling, the processes take place everywhere in the computational domain. The figure is divided into three separate steps, because the calculations of the reactions between the alkali metal compounds and the formation of the fine particles have been computed with the post-processing technique. In this technique, the results obtained from the combustion calculations, such as temperature distribution, are fixed when the equilibrium chemistry and particle formation calculations are being computed. This is possible because particle formation is not assumed to affect the flow or temperature field.

In the first part of the model, the alkali metal compounds enter the boiler furnace when the injection of black liquor takes place. The alkali metal compounds, depicted in the lower part of the furnace in Fig. 2, are assumed to be in their gaseous form when they enter the furnace. The trajectories and the combustion of black liquor droplets are modeled with ANSYS/FLUENT. The amount of the alkali metal compounds released from black liquor is calculated according to the average release values calculated in the dissertation of Mikkanen [7]. In reality, many factors affect the release of the compounds; therefore, the applied values are only approximations. For example, the release of sodium and potassium is temperature dependent [19,20]. Another significant factor to consider is that chlorine contributes to the release of alkali metals [3,21].

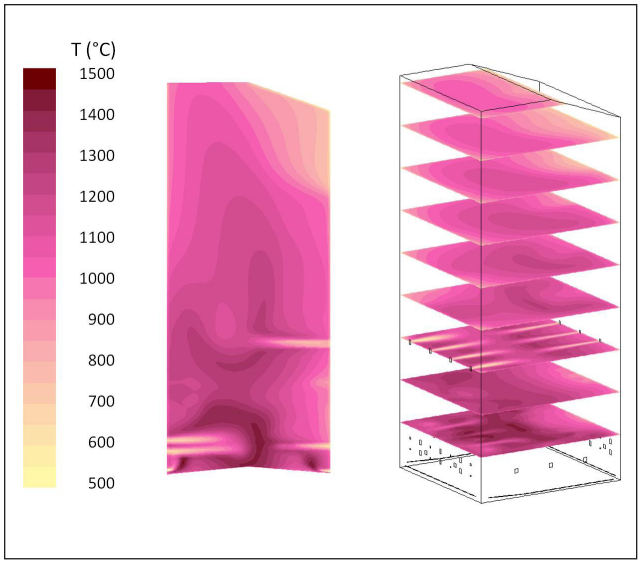
The second part of the modeling focuses on the reactions taking place between the gaseous alkali metal compounds [18]. These reactions are presented in the middle section of the furnace in Fig. 2. According to Jokiniemi [9] and Saw [17], an equilibrium chemistry assumption is sufficient for these reactions, and therefore FactSage can be used to calculate the equilibrium states in different computational cells. The states of the equilibrium reactions in each computational cell are affected by the specific mass fractions of sodium, potassium, and sulfur, together with the prevailing temperature. As a consequence, the varying conditions in different areas of the boiler furnace affect the modeling results.

The final part of the modeling considers the processes depicted in the upper part of the furnace. At first, new particle cores are formed by homogenous nucleation from sodium sulfate, which is the main compound in the fine fume particles [7,8]. After nucleation, the particle cores can grow as a result of condensation. The condensation involves sodium sulfate, sodium chloride, potassium sulfate, and potassium chloride. The final step in the particle formation process is coagulation, in which individual fume particles collide with each other and form new, larger spherical particles. The functions chosen for the particle processes in FPM are the Frenkel model for nucleation and the Dahneke model for coagulation [14]. The Kelvin effect, which accounts for the weaker stability of small particles, is not considered in the modeling. This is because the Kelvin effect causes computational instability and is not considered to have a significant effect on the results when the particles are more than 0.1 μm in size [22], as in this case. Moreover, because FPM assumes a log-normally distributed size for the particles, a fixed standard deviation of 1.5 is chosen for the size distributions to stabilize the calculations.

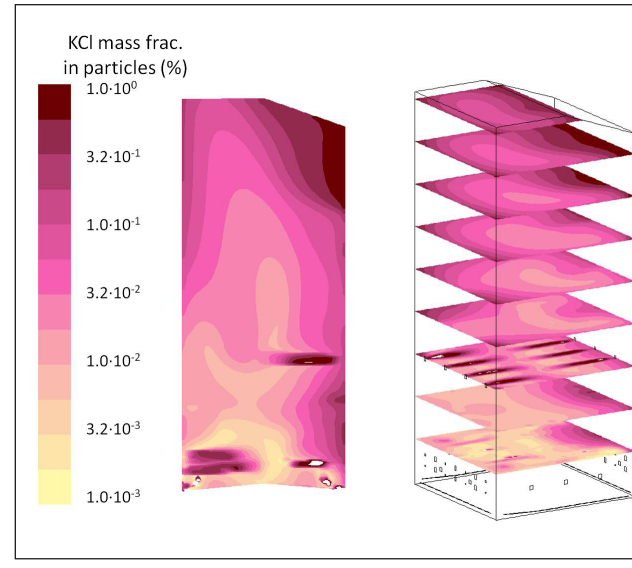
RESULTS AND DISCUSSION

We compared preliminary modeling results with data from similar studies. **Figure 3** shows the temperature distribution of the boiler furnace. This temperature distribution is obtained from the CFD simulation by modeling the combustion of black liquor. According to the combustion model, the areas of the lowest temperature in the boiler are located at the air inlets and below the nose arch. These are also the areas where, because of condensation, the fine particle growth is the fastest. To illustrate this, **Fig. 4** shows the total mass concentration of the fine particles in the boiler furnace.

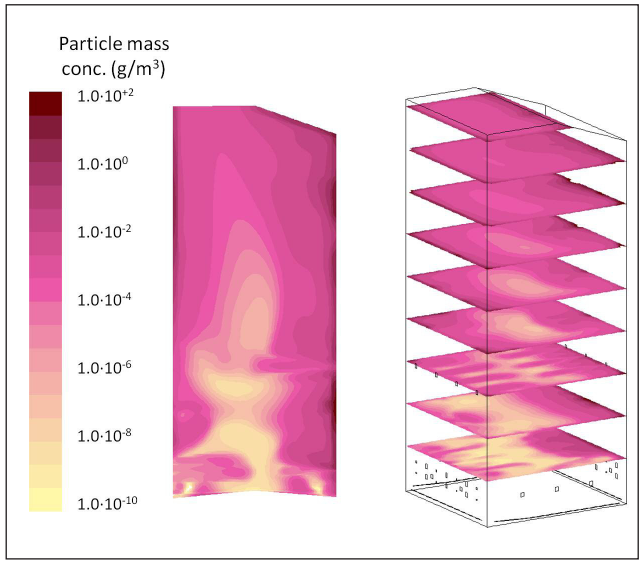
The total fine particle mass concentration presented in Fig. 4 is almost inversely proportional to the temperature distribution shown in Fig. 3. This is because condensation can only occur when the boiler temperature is low enough for the condensing species to saturate. Furthermore, condensation is the most important process affecting the particle mass distribution. The average volumetric total fine particle mass concen-



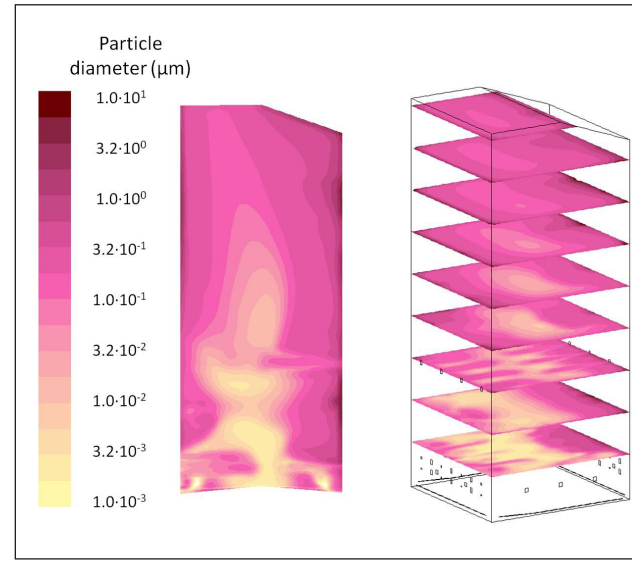
3. Temperature distribution in the boiler furnace.



5. The mass fraction of potassium chloride in the fine particles.



4. Total fine particle mass concentration.

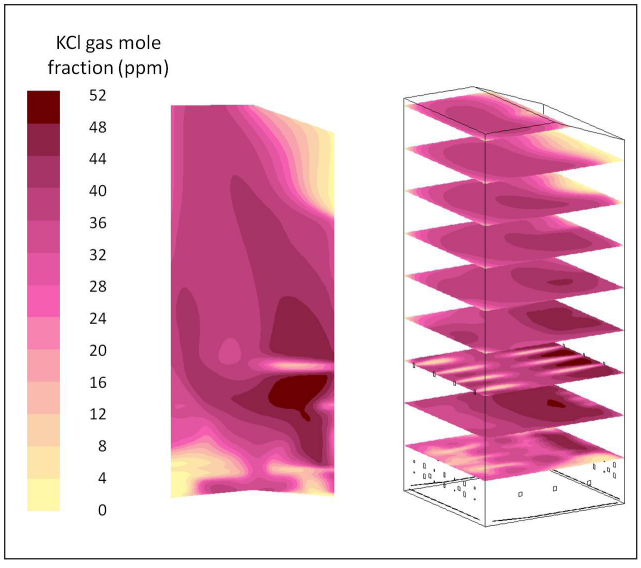


6. The geometric mean diameter of the fine particles.

tration in the boiler furnace given by the model is around 6 g/Nm³ in standard conditions (0ºC, 101.325 kPa). Unfortunately, we found no corresponding measurement values in the literature, but the values given by Mikkanen et al. [23] indicate that the mass concentration obtained with the help of the model is in the correct order of magnitude. The values of Mikkanen et al. give an approximation of 10 g/Nm³ for the fine particle (d_p < 3 µm) mass concentration at the electrostatic precipitator inlet. Moreover, because most of the alkali metal compounds condense in the superheater area, the modeled total fine particle mass concentration most likely would increase further when moving on from the furnace to the superheater.

Because different alkali metal compounds condense in different areas inside the furnace, the composition of the fine particles also is affected by the temperature distribution. As an example of the variation in particle composition, **Fig. 5** shows the mass fraction of potassium chloride in the fine particles. **Figure 6** presents the geometric mean diameter of the particles.

Figure 5 shows that the mass fraction of potassium chloride in the fine particles is highest in the upper section of the furnace. This is a result of the decrease in temperature and the difference in the equilibrium vapor pressures of alkali sulfates and alkali chlorides. Alkali chlorides have a higher equilibrium vapor pressure; therefore, they are able to condense only in the lower temperatures of the furnace. According to the modeling results, the mass fractions of sodium chloride and potassium chloride in the upper furnace are approximately 0.2% and 2%. Together, these values result in a chlorine mass fraction of around 1.2%. This value corresponds quite well with the typical enrichment factors for chlorine [1], and with



7. The mole fraction of gaseous potassium chloride.

the existing ash composition data based on similar liquors.

Because the condensation takes place mainly in the low temperature areas, the fine fume particles are largest near the furnace walls (Fig. 6). In the center of the furnace, the particles seem to be very small, but this is the result of new particle seeds being formed. The average fine particle diameter calculated by the model is 0.1-0.4 µm at different levels of the furnace. This value is in the same range with the values given by Mikkanen [7]. In her work, the diameters of the individual fume particles collected from the furnace and observed with the scanning electron microscope (SEM) also were between 0.1 µm and 0.4 µm. However, coagulation is a time-dependent process; therefore, the choice of calculation time affects the particle size distribution. As a consequence, the average diameter given by the model could change if the calculation time were different.

Figure 7 presents the distribution of gaseous potassium chloride in the boiler furnace. The mole fraction of potassium chloride at a cross-section of the furnace outlet is around 30 ppm, which is in the same range as the modeling results of Jokiniemi et al. [18]. The amount of gaseous potassium chloride is significantly lower in the areas of low temperature, because that is where the gaseous potassium chlorides condense onto the particles.

FUTURE RESEARCH

The next stage in developing the model is to conduct validating measurements in a full-size kraft recovery boiler and in a small pilot facility. The pilot facility enables investigating the formation of fume particles from the gaseous alkali metal compounds in more detail, and with carefully controlled boundary conditions. Moreover, the model parameters can be adjusted according to the validating measurements. The nucleation function in the FPM, in particular, is known to give inaccurate results for particle number concentration and should be readjusted [16,24].

In addition to the validating measurements, the modeling method itself must be further improved. A new modeling approach is needed when the formation of sodium and potassium carbonate is added to the model, because new equilibrium reactions have to be used. Furthermore, because the choice of the calculation time affects the particle coagulation results, the modeling of coagulation should be investigated in more detail. In the future, the model will also be extended to the superheater area of the boiler, which is the most critical area in terms of fouling and corrosion in a modern kraft recovery boiler. **TJ**

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ABOUT THE AUTHORS

The problems of fouling and corrosion have not been overcome in kraft recovery boilers. We wanted to get an insight to this problem through modeling the behavior of alkali metal compounds in the boilers.

The modeling method we presented differs from previous work in that it simulates the aerosols in three dimensions with the Fine Particle Model (FPM) software for the first time. As a result, the method can predict the local distributions of alkali metal compounds in gas and particle phases.

Because there is hardly any experimental data available related to the behavior of alkali metals in the kraft recovery boiler furnace, validation of the modeling results was difficult. However, the model will be compared with new measurement results in the future.

From this study, we learned that the modeling of fine particle formation is possible with the help of FPM, although fine particle formation is a complicated process. However, the modeling of condensation was rather straightforward, so a good prediction for particle composition and mass could be obtained.

When the modeling method is further developed, it can be used as a tool in boiler design to avoid corrosion. Additionally, mills might use it in for planning optimal operating conditions.

Our next step is to perform validative measurements in an actual kraft recovery boiler and develop the modeling method further by adding reactions for alkali carbonates.

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