33rd Oil Shale Symposium

Pyroprocessing of oil shale – chemistry and mineralogy related fouling issues

Dr. Alexander Lojewski
ThyssenKrupp Resource Technologies GmbH
Process Engineering Department

UMATAC Industrial Processes
A company of ThyssenKrupp Resource Technologies

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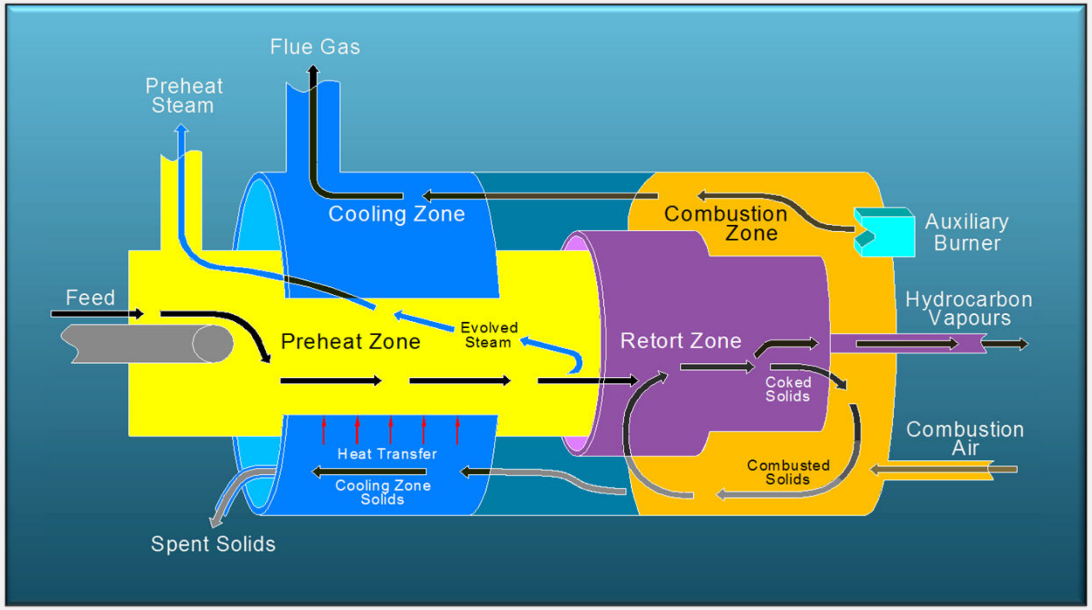
Basic concept of the ATP Processor

	Preheat	Retort	Combustion	Cooling
Residence Time/Cycle (min)	10-15	5-8	6-12	10-20 Coarse, <1 Fines
Temperature (°C)	Amb. – 250	500	680-750	650-350
Gas Phase	Steam	HC Vapors	Air/F.G./Dust	F.G./Dust
Pressure (mmWC)	-2	-40	-15	<-15
Carbonate Rxns Intensity	N/A	Low	High	Moderate - Diminished Rate

ATP Fushun, PRC



Operating conditions during oil production

Three operations on oil shale

1st Oil: 08/26/2013, total feed rate approx. 130 t/h

2nd Oil: 09/03/2013, total feed rate 130 t/h – 160 t/h

3rd Oil: 10/03/2013, total feed rate approx. 130 t/h

!

Total feed rate approx. 70 % of maximum feed capacity

Feed composition during oil shale operation:

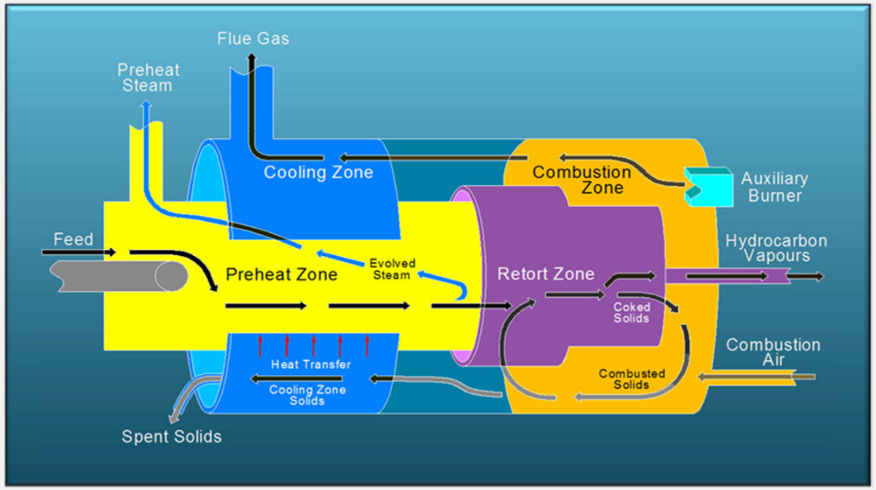
- 30-40 % of inert
- 60-70 % of Fushun Mining Group West Pit Oil Shale
- Moisture content of feed > 16 % (data provided by FMG)

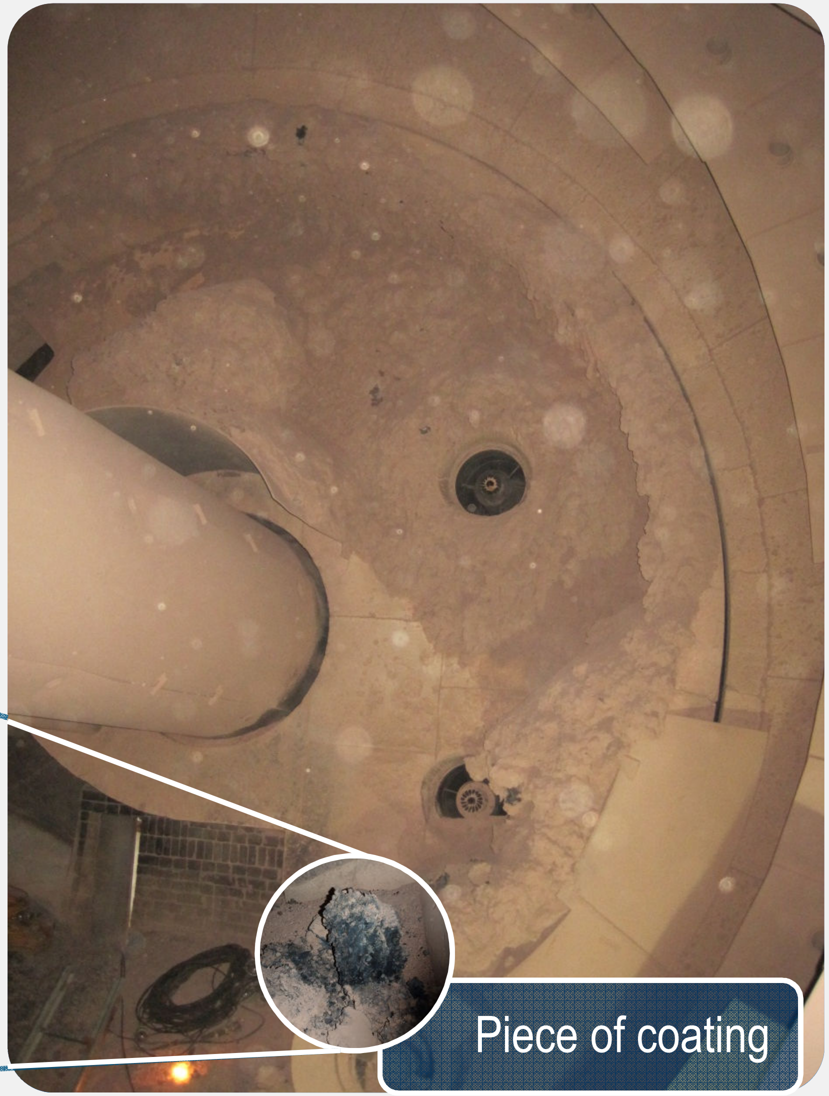
Burners kept in operation during commissioning on oil shale

- to allow for quick adjustments in case of process upsets.
- to complete commissioning and to improve reliability on them.

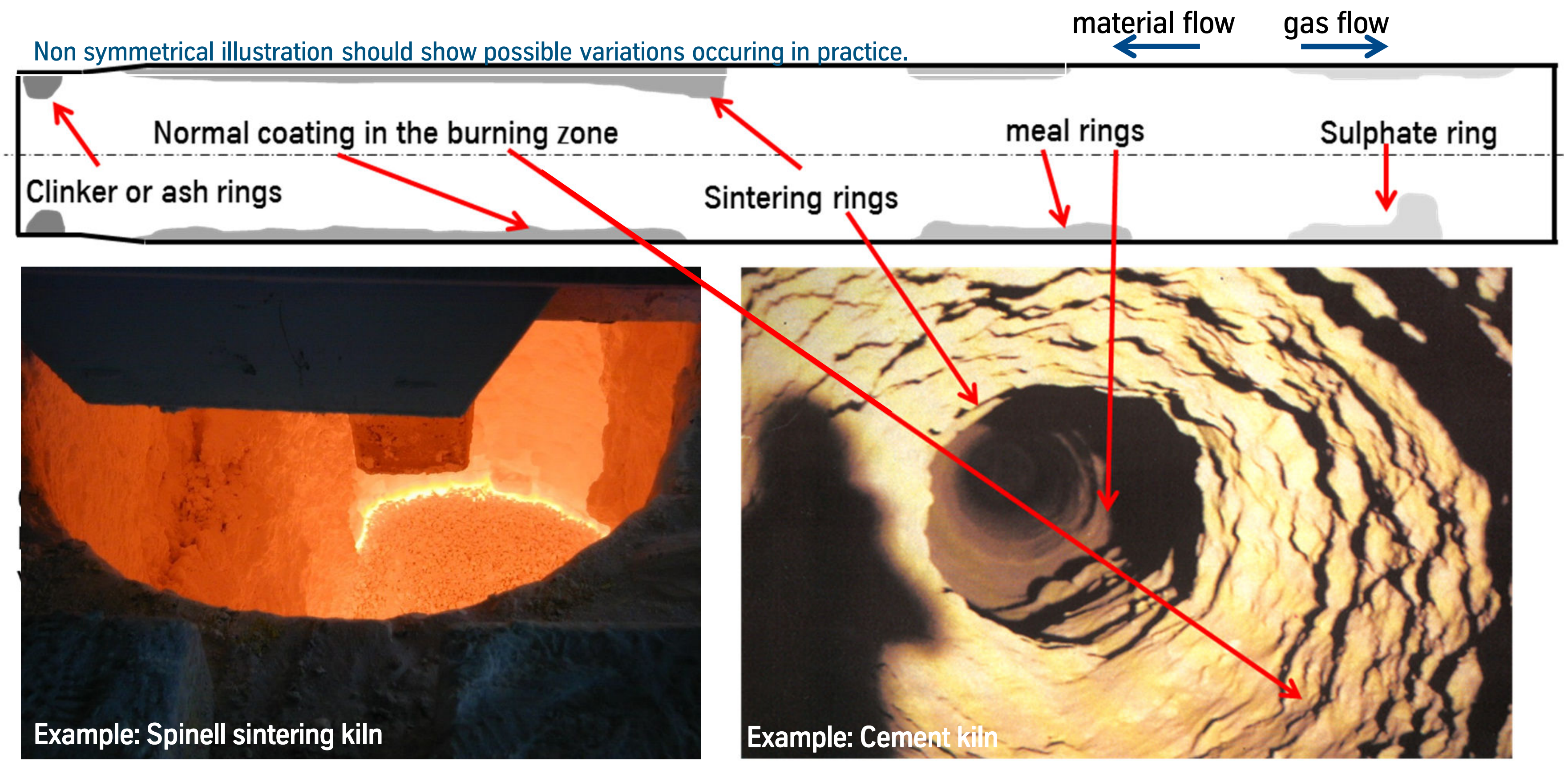
Permanent operation of auxiliary burners only during commissioning on oil shale !

Phenomenon during oil production: Coating around the auxiliary burners





Coating is a well-known process in cement and minerals plants

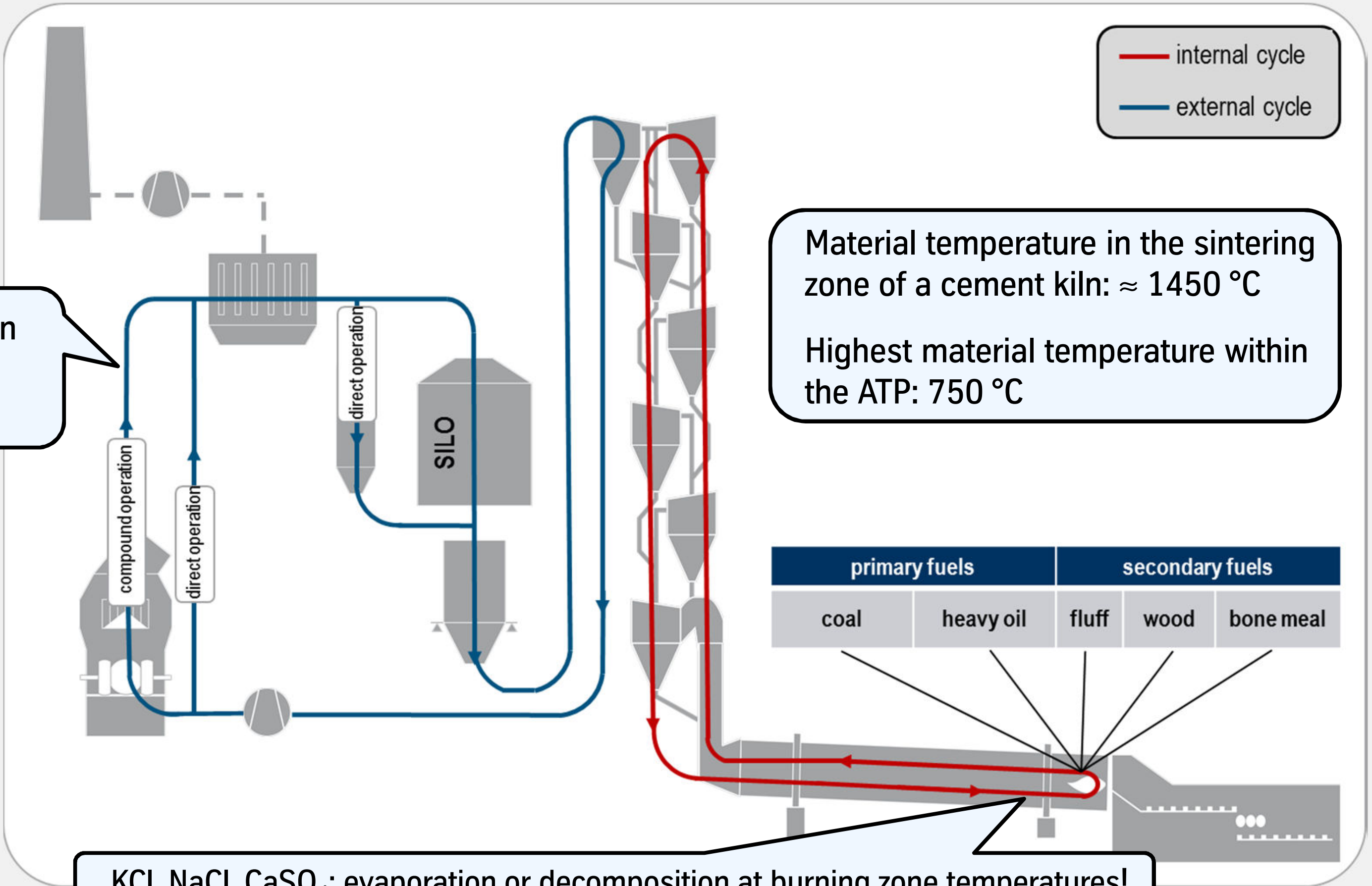


Ring formation in a cement kiln causes restrictions in gas and material flows.

Causes for coating in the cement industry

Impurities (alkali salts, chlorine, sulphates) entering the kiln system with raw materials and fuel become volatile under the thermal conditions of the burning zone. With the countercurrent flow of gas and material gaseous impurities are transported to colder regions where they condensate.

FeS, FeS_2, Hg: evaporation or decomposition at preheater temperatures!



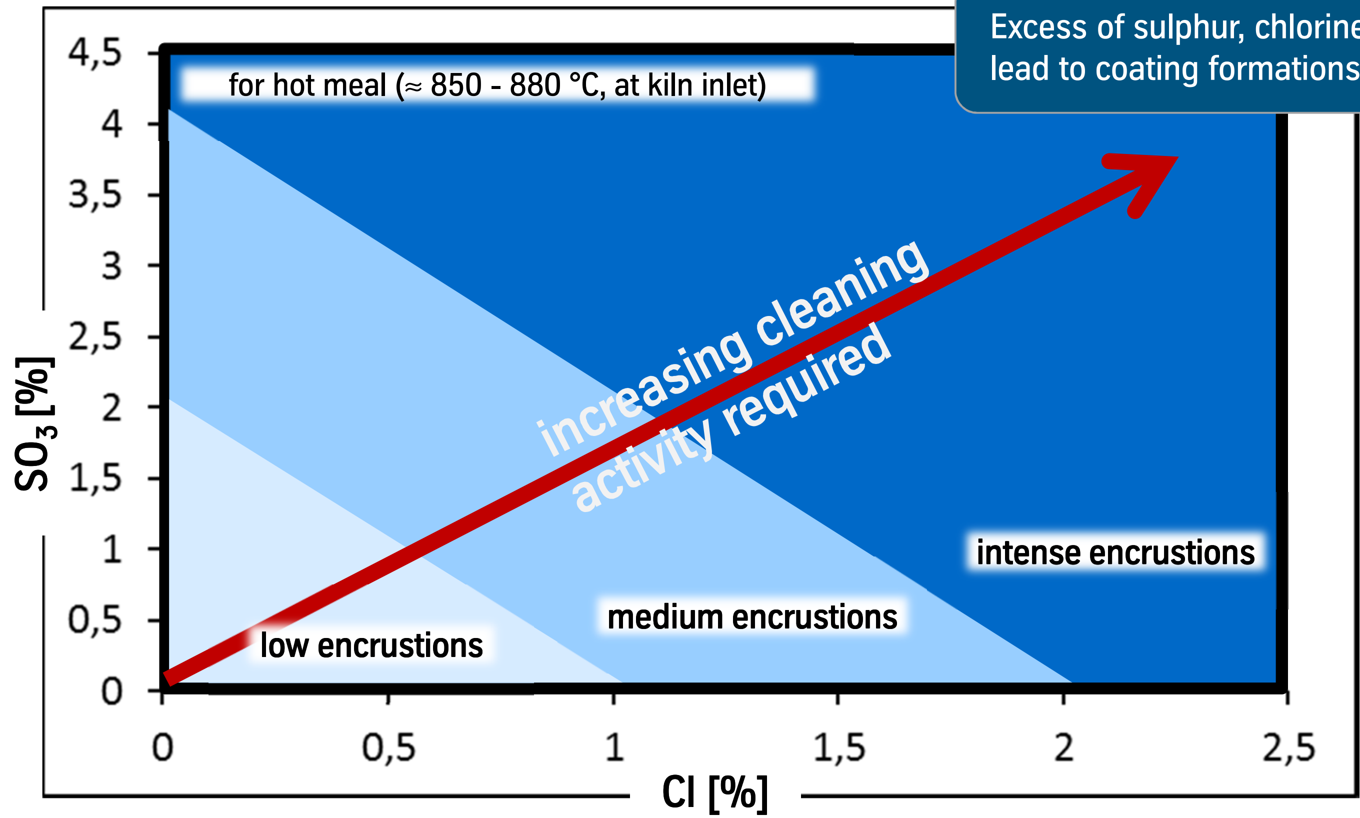
Material temperature in the sintering zone of a cement kiln: ≈ 1450 °C

Highest material temperature within the ATP: 750 °C

KCl, NaCl, $CaSO_4$: evaporation or decomposition at burning zone temperatures!

Conditions for coating formation at the kiln inlet, riser duct, calciner

Excess of sulphur, chlorine and/or alkali will lead to coating formations



$$Q_{SO_3/Alkalis}[Kiln\ Feed] = \frac{\frac{SO_3}{80}}{\frac{Na_2O}{62} + \frac{K_2O}{94} - \frac{Cl}{71}}$$

Q=1	Sulphur and alkalis in balance
Q>1	Sulphur excess
Q<1	Alkali excess

Chemical analysis of West Pit Oil Shale, Fushun Mining Group

Material	Inert (red), feed belt	Oil shale pure feed belt	Slag, combustion end	Ash, oil shale operation, ash belt
Date	3-Sep-13	3-Sep-13	30-Aug-13	3-Sep-13
Time	7:28	7:28		10:00
% LOI at 1050°C	5,00	20,69	0,05	5,29
% SiO_2	58,43	49,15	62,62	58,84
% Al_2O_3	20,25	17,01	21,03	20,21
% TiO_2	1,15	1,03	1,16	1,13
% Fe_2O_3	9,44	7,51	9,59	9,30
% Mn_2O_3	0,14	0,11	0,14	0,14
% CaO	1,54	1,05	1,63	1,32
% MgO	1,74	1,29	1,56	1,56
% SO_3	**1,05**	**1,26**	**0,31**	**1,09**
% P_2O_5	0,28	0,22	0,31	0,27
% Na_2O	0,70	0,64	0,93	0,93
% K_2O	1,13	0,75	0,74	0,96
% Cl^-	**0,002**	**0,003**	**0,005**	**0,005**
% Sum	100,852	100,713	100,025	101,045

The sulphur to chlorine ratio does not reveal any cause for the coating found around the burners at the combustion end frame.

$$Q_{SO_3/Alkali}[Shale] = 0.86$$

$$Q_{SO_3/Alkali}[Inert] = 0.56$$

Both feed materials show an surplus of alkalis.

But the fuel oil contains 0.54 % of sulphur reducing the alkali excess.

The chemical composition of the feed material and fuel does not entirely explain the amounts of coating found.

Mineralogical changes as an indicator for thermal stress of solid material

Mineral name and formula	Sample	Inert (red), feed belt	Oil shale feed belt	Ash, oil shale operation, ash belt	Slag, combustion end
Date		3-Sep-13	3-Sep-13	3-Sep-13	30-Aug-13
Time		7:28	7:28	10:00	
% Quartz	SiO_2	41,9	21,8	34,8	26,6
% Crystobalite	SiO_2	16,7	4,2	7,8	**19,8**
% Muscovite	$KAl_2AlSi_3O_8(OH)_2$	11,7	23,6	25,8	
% Orthoclase	$KAlSi_3O_8$	5,1	5,0	7,2	2,1
% Plagioclase	$(Na,Ca)(Al,Si)_3O_8$	13,3	5,9	15,2	3,1
% Kaolinite	$Al_2Si_2O_5(OH)_4$		31,5		
% Pyrite	FeS_2		0,8		
% Magnetite	Fe_3O_4			5,6	1,8
% Hematite	Fe_2O_3	8,5	0,3	1,2	1,8
% Anhydrite	$CaSO_4$			0,8	
% Gypsum	$CaSO_4 \cdot 2H_2O$	2,9	1,0	1,6	
% Siderite	$FeCO_3$		6,0		
% Mullite	$Al_{(4+2x)}Si_{(2-2x)}O_{(10-x)}$				**28,1**
% Cordierite	$Mg_2Al_4Si_5O_{18}$				**6,6**
% Hercynite	Fe_2AlO_4				**10,2**
	Sum [%]	**100,0**	**100,0**	**100,0**	**100,0**

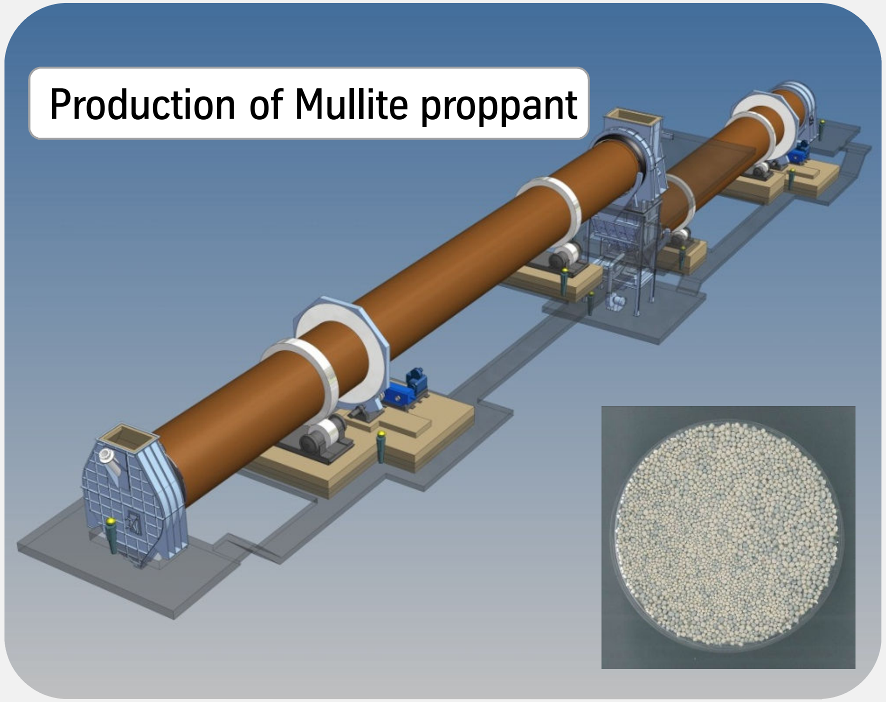
missing increasing

Experiences from proppant production facilities

Mineral name and formula		Oil Shale	Feed Proppant
% Quartz	SiO_2	21.8	26.7
% Crystobalite	SiO_2	4.2	
% Muscovite	$KAl_2AlSi_3O_8(OH)_2$	23.6	26.1
% Orthoclase	$KAlSi_3O_8$	5.0	4.3
% Plagioclase	$(Na,Ca)(Al,Si)_3O_8$	5.9	
% Kaolinite	$Al_2Si_2O_5(OH)_4$	31.5	33.8
% Pyrite	FeS_2	0.8	
% Magnetite	Fe_3O_4		
% Hematite	Fe_2O_3	0.3	5.6
% Anhydrite	$CaSO_4$		
% Gypsum	$CaSO_4$*$2H_2O$	1.0	
% Siderite	$FeCO_3$	6.0	
% Mullite	$Al_{(4+2x)}Si_{(2-2x)}O_{(10-x)}$		
% Cordierite	$Mg_2Al_4Si_5O_{18}$		
% Hercynite	Fe_2AlO_4		
% Anatase	TiO_2		3.6
		100.0	100.1

In cement plants the presence of iron increase the amount of liquid phase formed (at 1400 °C) in the sintering zone :

$$\%LP = 2{,}95 \times \%Al_2O_3 + 2{,}2 \times \%Fe_2O_3 + \%MgO + \%Na_2O + K_2O$$



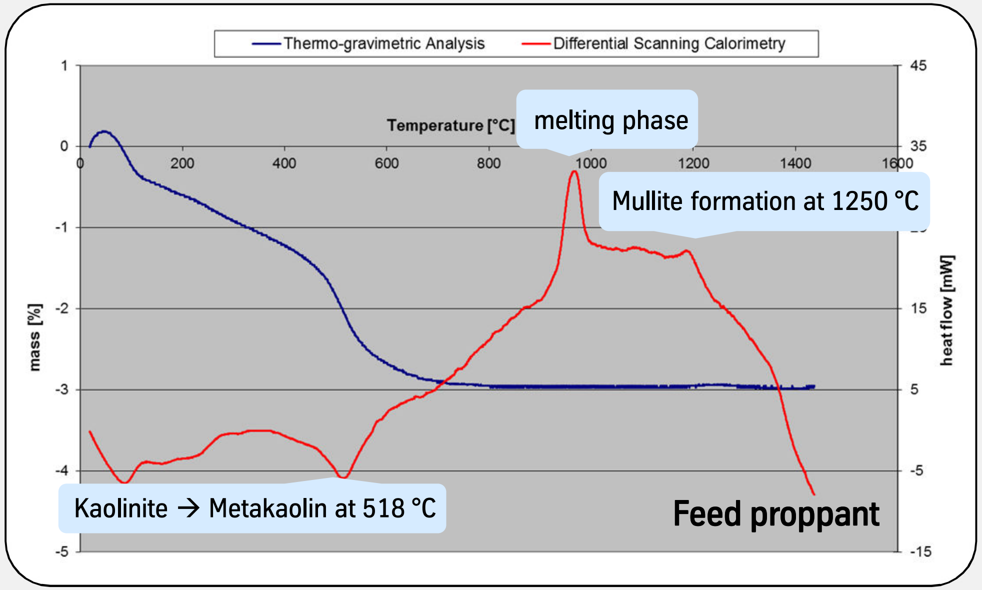
Kaolinite to Metakaolin

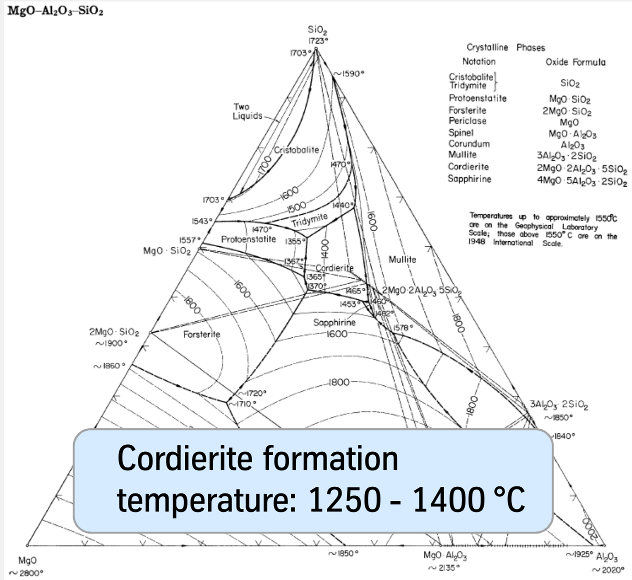
$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O_g$$

Metakaolin to Mullite

$$3(Al_2O_3 \cdot 2SiO_2) \rightarrow 3Al_2O_3 \cdot 2SiO_{2,(s)} + 4SiO_2$$

Mineralogical changes as an indicator for thermal stress of slag material





Source: Osborn & Muan, 1960. Phase equilibirum diagrams in oxid systems. The American Ceramic Society, Columbus

Reactions of Muscovite:

- 550 – 750 °C Dehydroxilation (Guggenheim et. al. 1988)
- 800 – 1000 °C Solid phase changes into Mullite, K-feldspar and a melt.

Reaction of $CaSO_4$:

$$CaSO_4 \rightarrow CaO + SO_2 + 0.5O_2$$

Taking place at T > 1200 °C

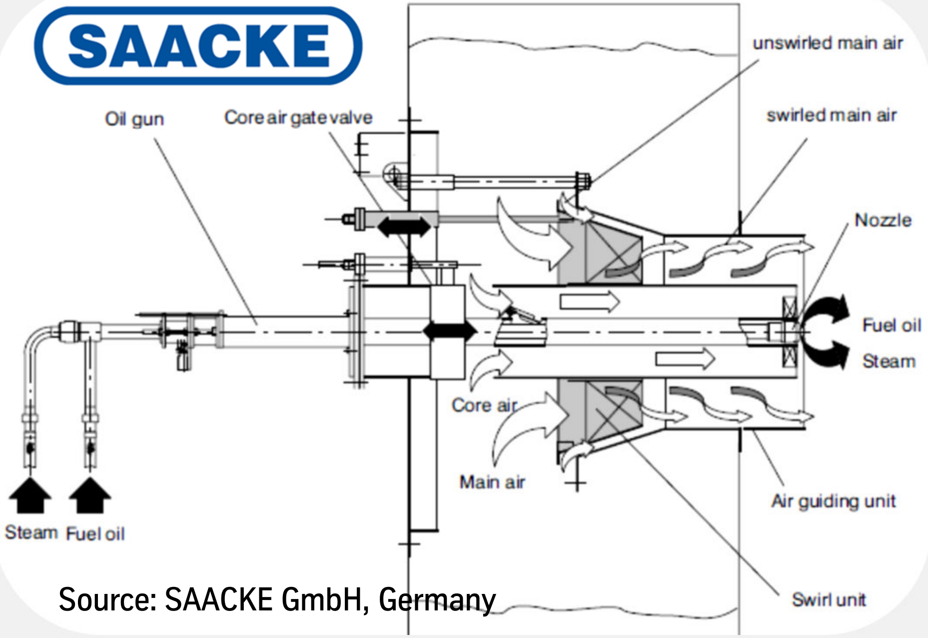
Conclusion

The presence of Mullite and Cordierite in the slag as well as the absence of calcium sulfates indicate that the coating forming material was heated above 1200 °C due to a direct contact to the burner flames

Saacke Duoblock Burner DDZ 10 – auxiliary burners

Technical data

- *Capacity (MW):*	4.4 – 13.3
- *Oil flow (heavy oil) (kg/h):*	389 – 1168
- *Combustion airflow (Nm³/h):*	5,500 – 16,400
- *Injection atomizer:*	*pressurized steam*
- *Ignition:*	*gas-electric*

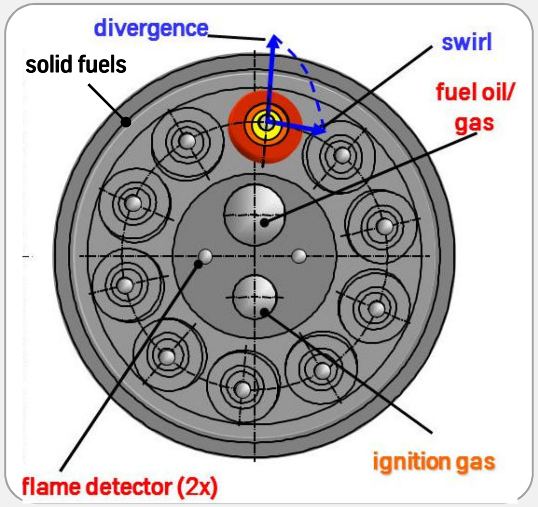


Source: SAACKE GmbH, Germany

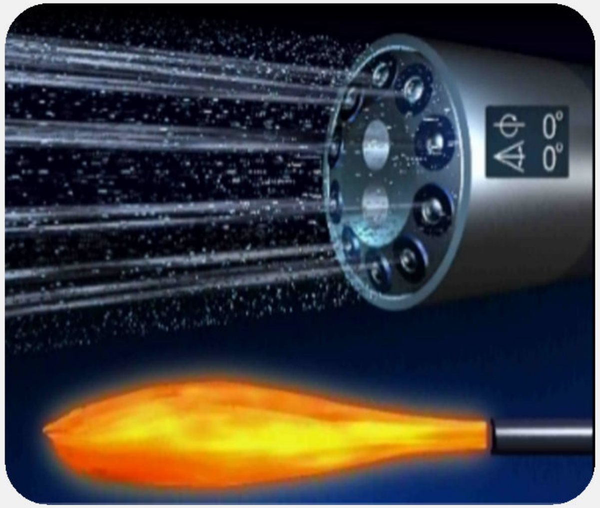
Adjusting swirl – experiences from POLFLAME VN operations

<u>POLFLAME VN main burner for rotary kilns:</u>

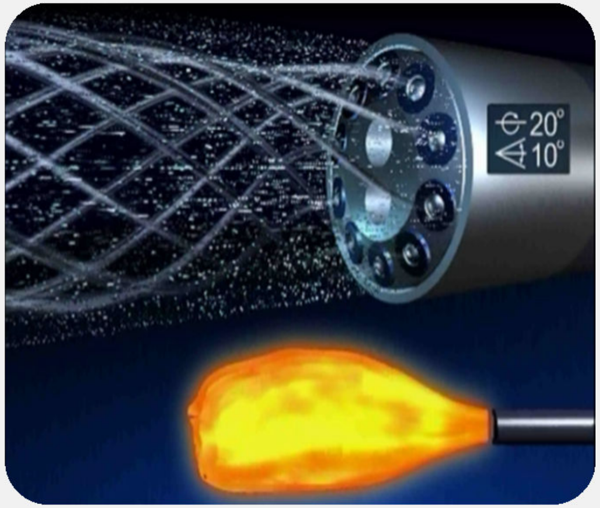
- **High speed nozzles for the injection of primary air**
- **Optimum mixture of different fuel types with secondary air**
- **Optimum flame shape adjustment**
- **Rugged design of the flow adjustment**
- **Long lifetime and operability**



Less swirl: long and weak flame



More swirl: short and hot flame



Summary and conclusions

Summary

- Coating is only found in the vicinity of the burner.
- Coating is not entirely reducible to the chemical composition of the feed.
- Coating takes place due to the high amount of clay minerals in the feed.
- The mineralogical composition of the coating material shows high temperature phases (Mullite, Cordierite, Hercynite).

Conclusions

- Adaption of burner settings.
- Installation of shock blowers like they are used in cement plants.
- No adjustment in feed chemistry required.
- **Under normal operation conditions of the ATP coating will not appear!**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