APPLYING THERMO 350M UNDERGROUND A FACTSAGE$^{\text{TM}}$ EQUILIBRIUM STUDY FOR UNDERGROUND COAL GASIFICATION

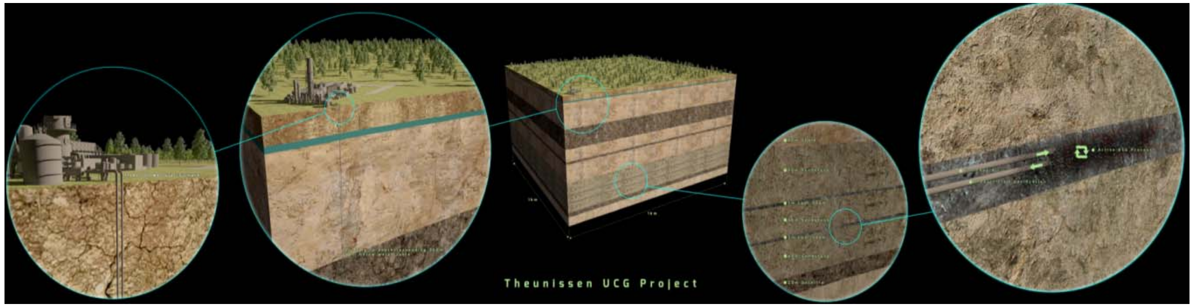
AFRICARY
African Carbon Energy

GTT Workshop, Aachen, Germany, July 2014

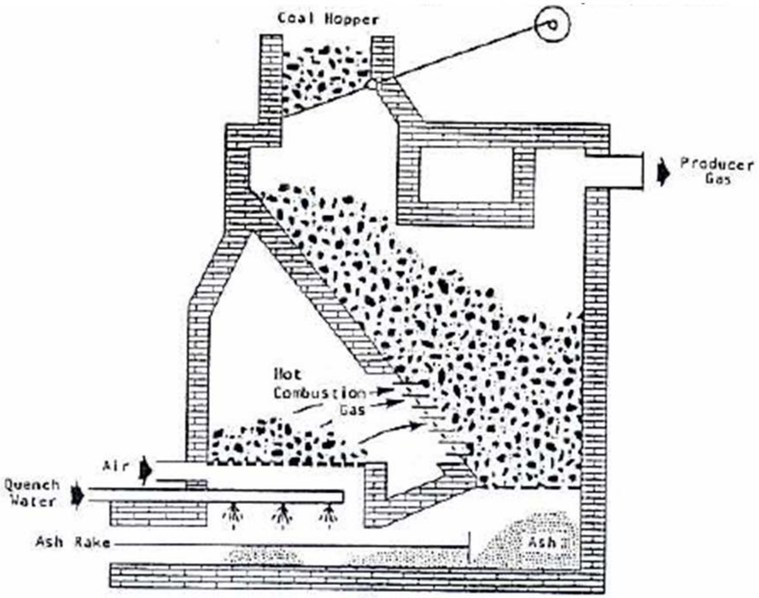
Dr. Johan van Dyk, Technology Manager, African Carbon Energy,
johan.vandyk@africary.com
Prof. Frans Waanders, North-West University
Mr. Johan Brand, CEO, African Carbon Energy

Roadmap of presentation

1. What is Underground Coal Gasification UCG?
2. Gasification Technology Overview
3. Building a model for a FACTSAGE$^{\text{TM}}$ Equilibrium Simulation
4. Mineral matter slag formation in the cavity
5. Trace element speciation – from 350m underground to surface treatment

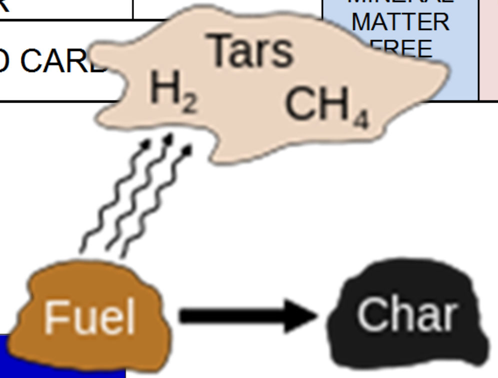


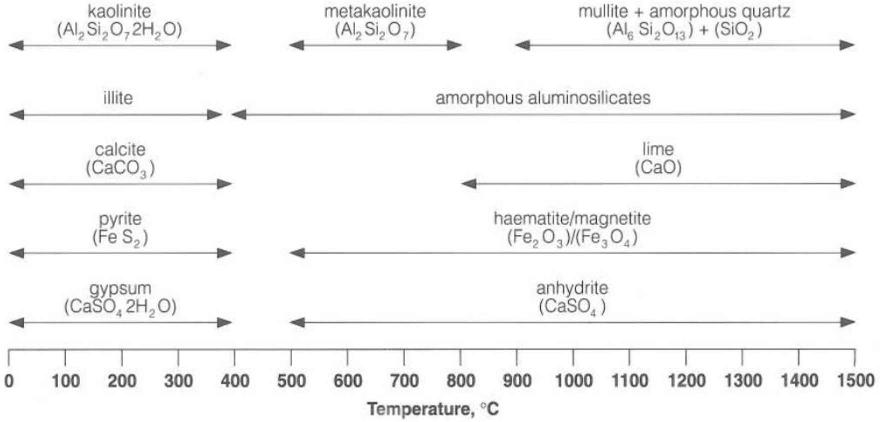
What is UCG?


Coal Hopper
Producer Gas
Hot Combustion Gas
Air
Quench Water
Ash Rake
Ash

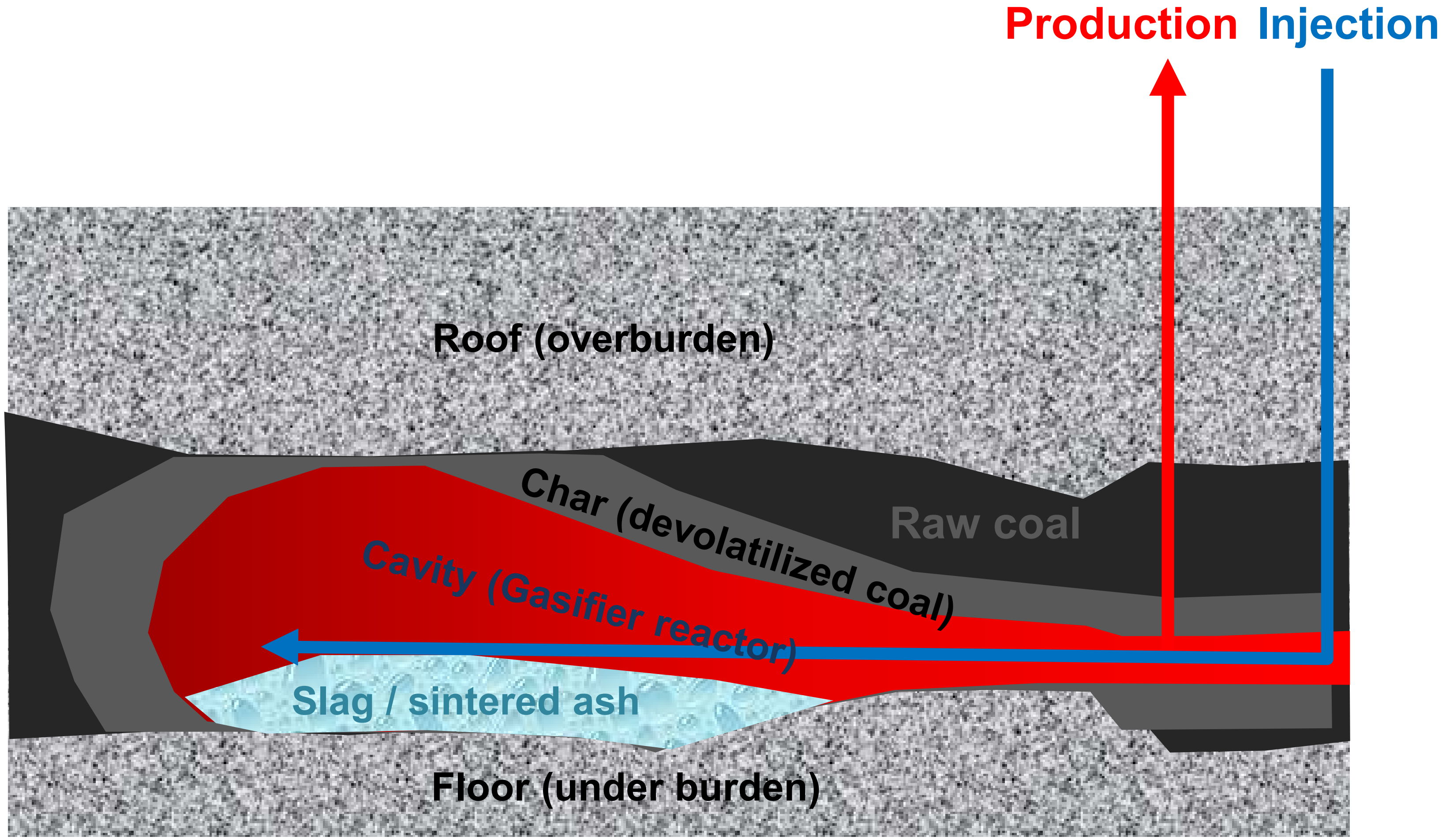
What is Underground  Gasification?

TOTAL MOISTURE	SURFACE MOISTURE						AS RECEIVED (ar)
	INHERENT MOISTURE					AIR DRIED (ad)	
MINERAL MATTER	ASH				DRY BASIS (db)		
	VOLATILE MINERAL MATTER	VOLATILE MATTER		DRY, ASH FREE (daf)			
PURE COAL	VOLATILE ORGANIC MATTER		DRY, MINERAL MATTER FREE				
	FIXED CAR						

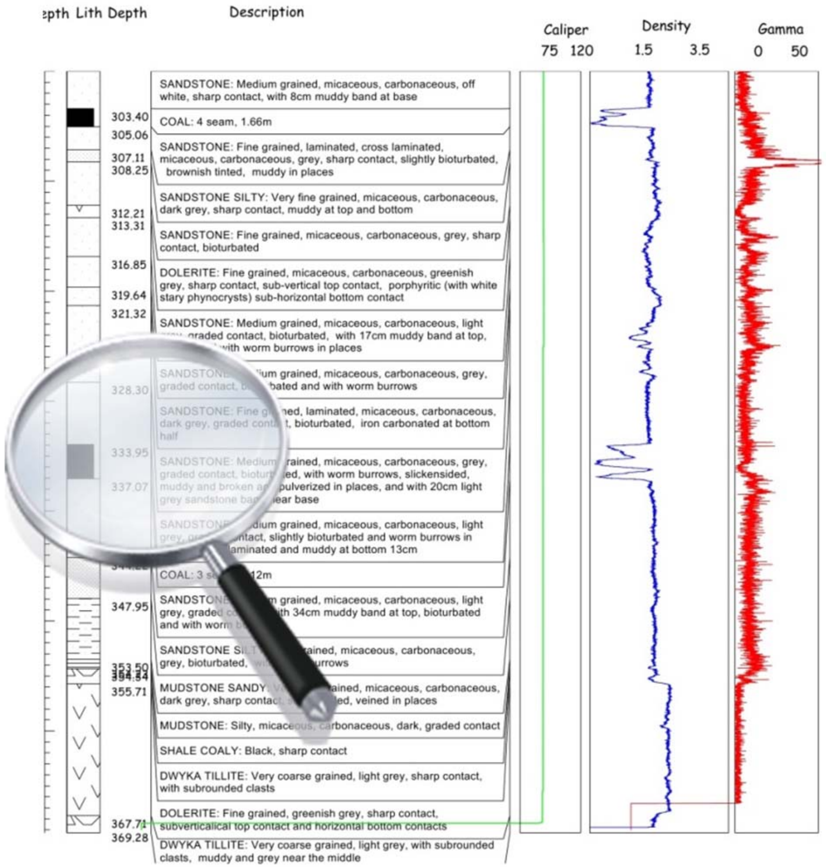


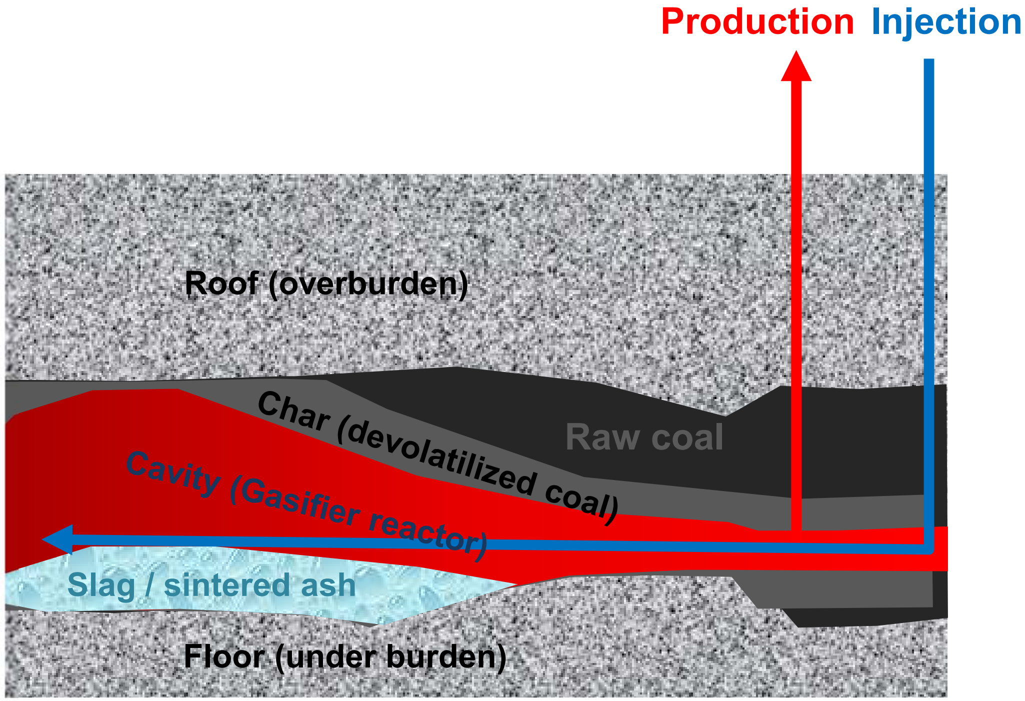


What is Underground Gasification?

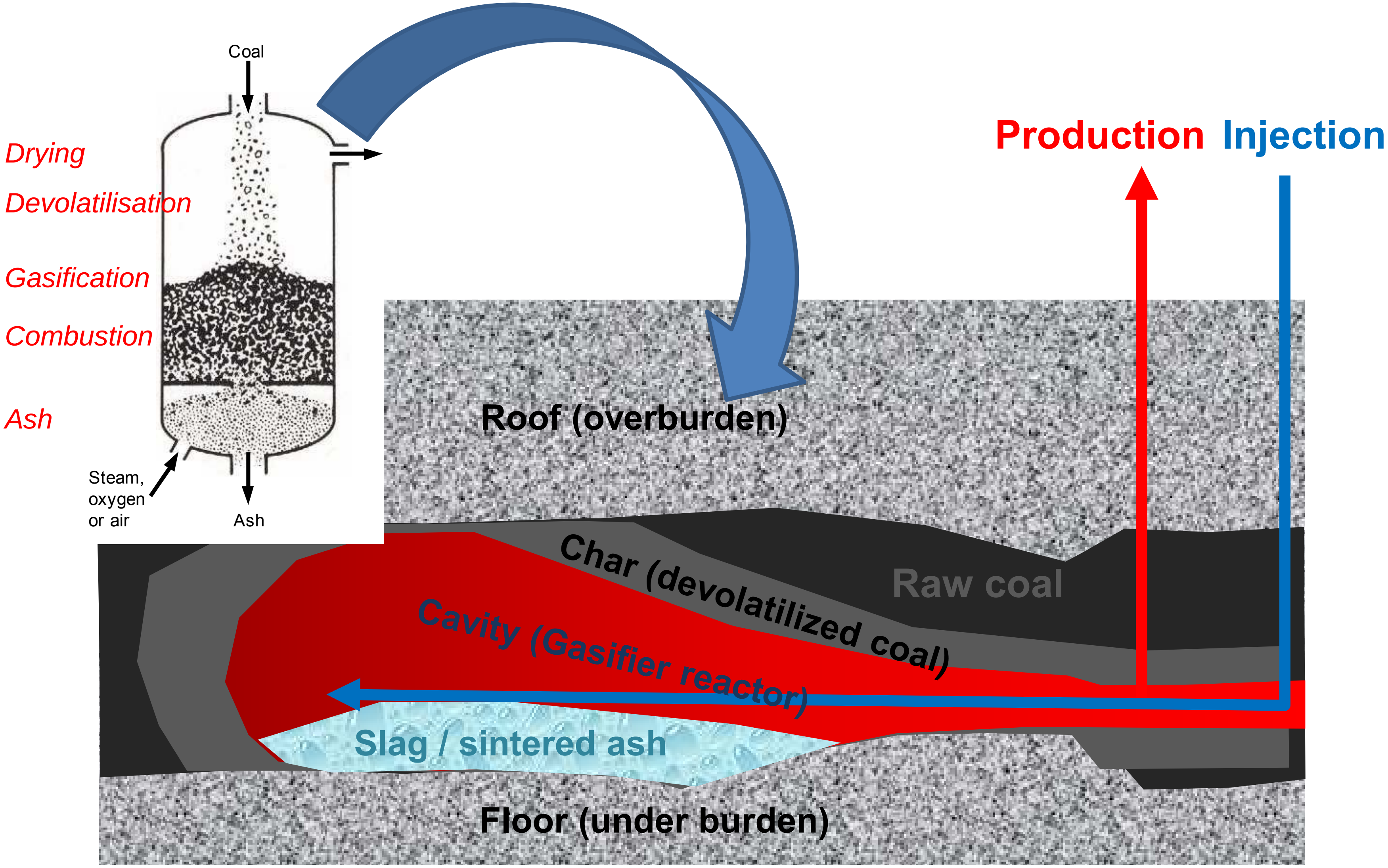


What is Underground  Gasification?

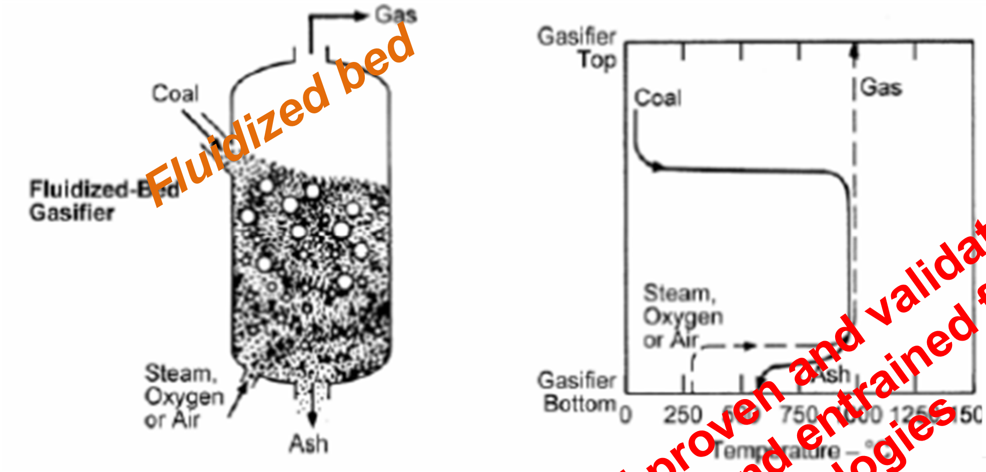




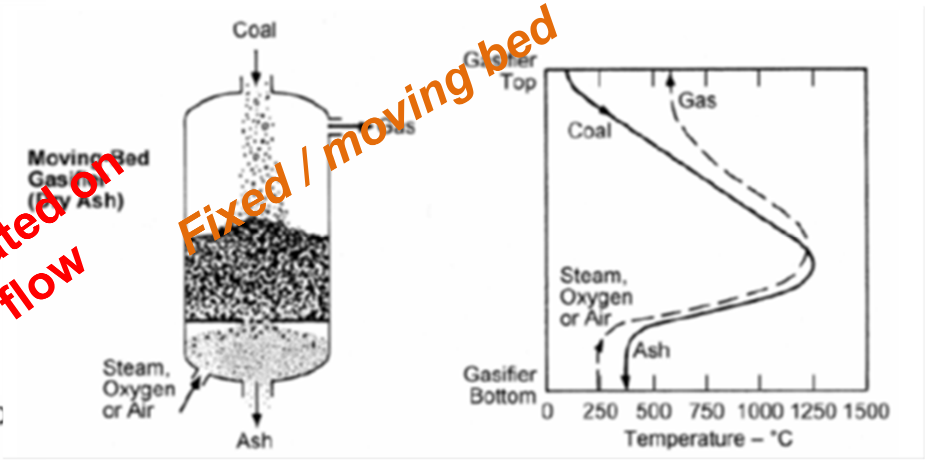
UCG is thus nothing strange!



Gasification Technology Overview

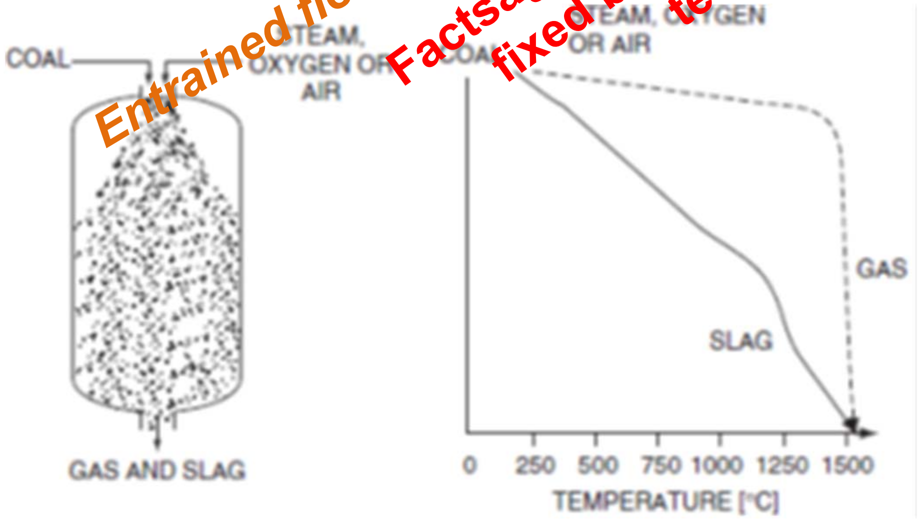


Fluidized bed

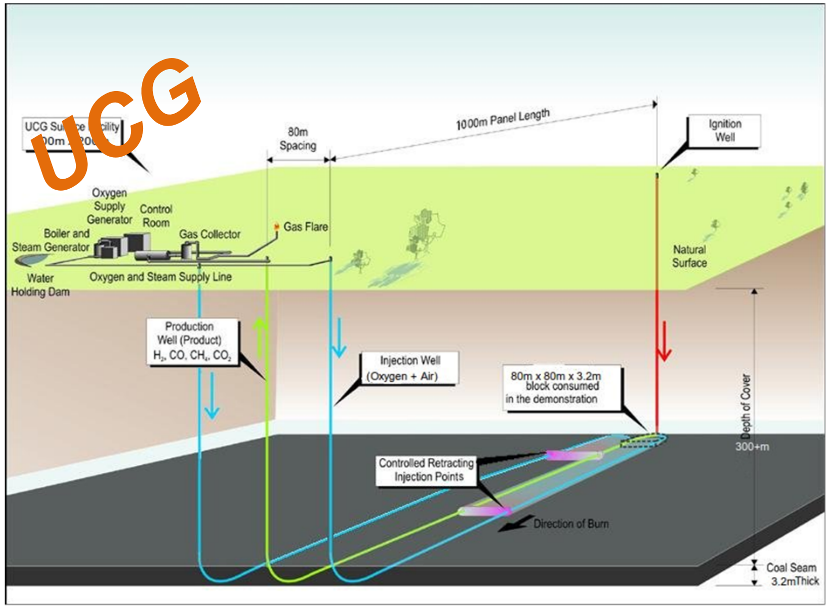


Fixed / moving bed

Factsage™ proven and validated on fixed bed and entrained flow technologies



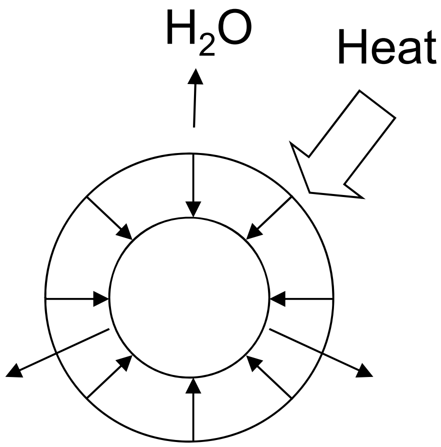
Entrained flow



UCG

Gasification Technology Overview (cont.)

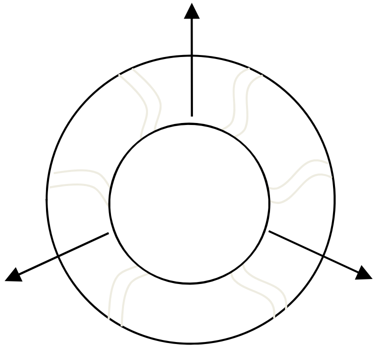
Heating and Drying



Thermal front penetrates particle

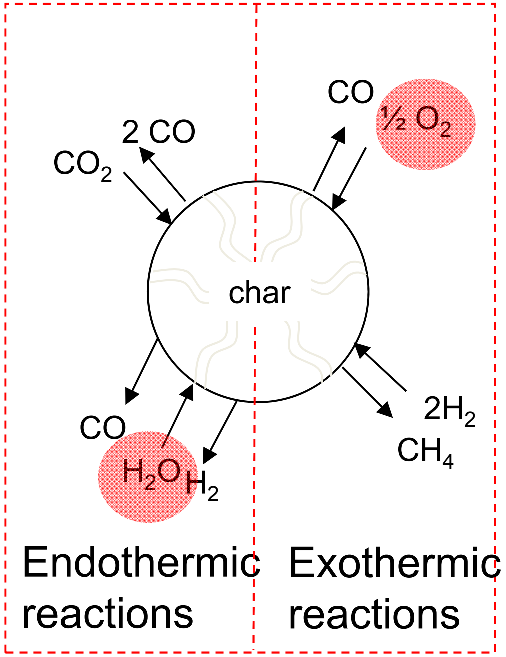
Pyrolysis

Volatile gases:
CO, CO_2, H_2, H_2O,
Light hydrocarbons, tar



Porosity increases

Gas-Solid Reactions



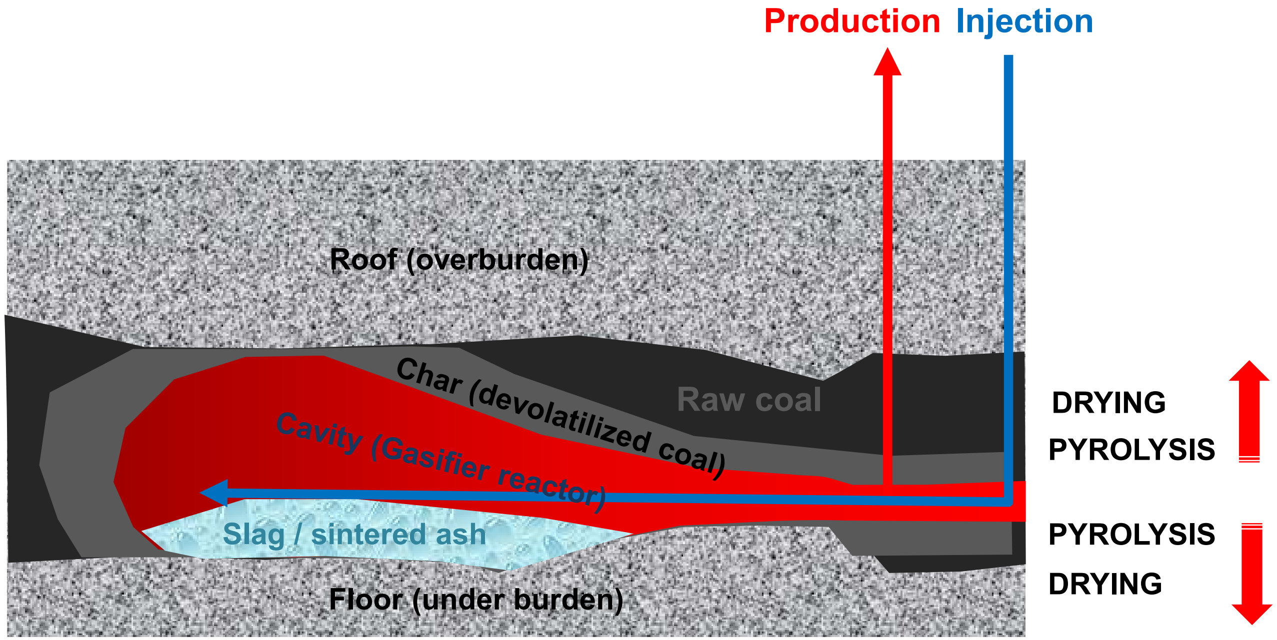
Gas-phase Reactions

$CO + H_2O \rightarrow CO_2 + H_2$

$CO + 3H_2 \rightarrow CH_4 + H_2O$

the science is the same

Building a model for a FACTSAGE™ Equilibrium Simulation



COMBUSTION ➡ **GASIFICATION** ➡ **PYROLYSIS** ➡ **DRYING**

$C + ½ O_2 \rightarrow CO$

$C + O_2 \rightarrow CO_2$

$H_2 + O_2 \rightarrow H_2O$

$C + CO_2 \rightarrow 2 CO$

$C + H_2O \rightarrow CO + H_2$

Water-gas shift:

$CO + H_2O \rightarrow CO_2 + H_2$

Methane formation:

$C + 2 H_2 \rightarrow CH_4$

$CO + 3H_2 \rightarrow CH_4 + H_2O$

$3C + 2H_2O \rightarrow CH_4 + 2 CO$

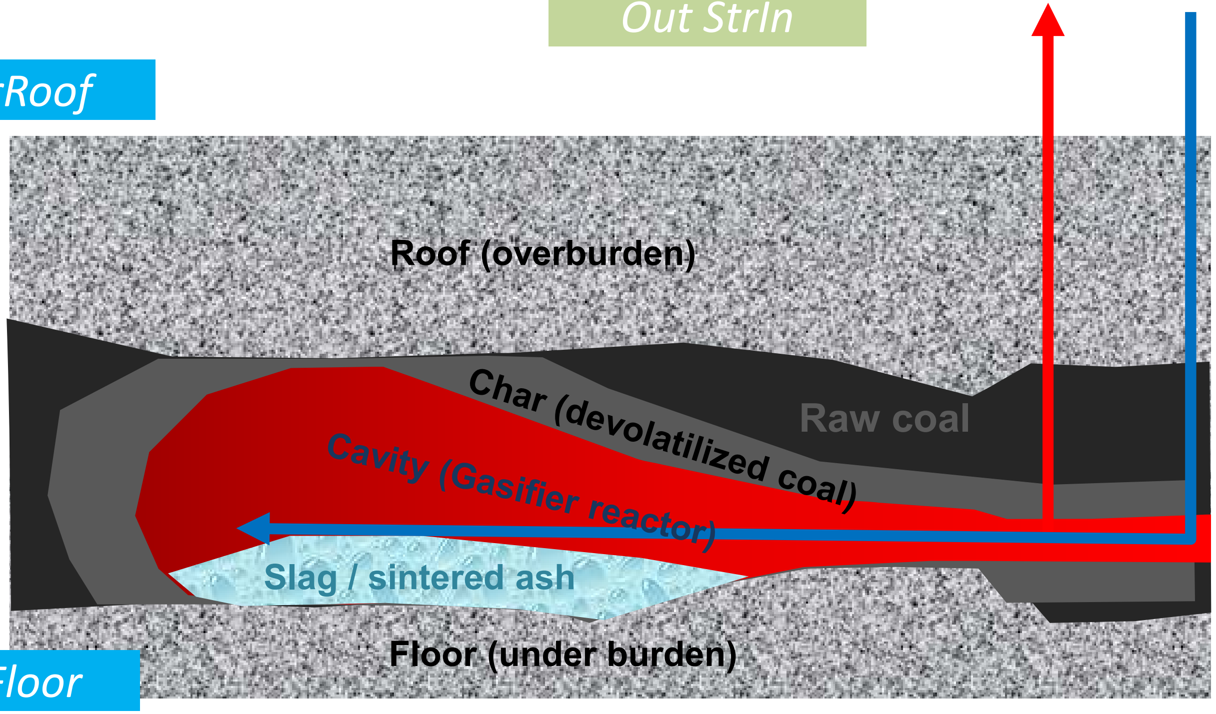
Building a model for a FACTSAGE^{TM} Equilibrium Simulation

AFRICARY

Out StrOrg

Out StrIn

In StrRoof



In StreamCoal

InStreamAir

InStreamO2

InStreamH2O

InStreamRecy

DRYING

PYROLYSIS ↑

PYROLYSIS ↓

DRYING

In StrFloor

COMBUSTION → **GASIFICATION** → ~~**PYROLYSIS**~~ → **DRYING**

Out StrComb

$C + ½ O_2 \rightarrow CO$

$C + O_2 \rightarrow CO_2$

$H_2 + O_2 \rightarrow H_2O$

In StrC

$C + CO_2 \rightarrow 2 CO$

$C + H_2O \rightarrow CO + H_2$

BypassStrC

Out StrSlag

INCLUDED

NOT YET

Building a model for a FACTSAGE^{TM} Equilibrium Simulation (cont.)

PROXIMATE (AR)	**Mass %**
Moisture	4.7
Fixed carboon	45.3
Volatile matter	21.4
Ash	28.6
	100.0
ULTIMATE (DAF)	
C	78.9
H	4.3
N	2.1
S	0.9
O	13.9
	100.1

Property	*Mass %*
H_2O	2.9
H_2	0.15
CH_4	4.01
CO	0.98
CO_2	7.2
N_2	2.1
Tar and oils	5.6

Scaling to 100 units of ash

ASH OXIDES (%)		**Trace Elements**	**mg/kg**	**% of ash**
SiO_2	52.7	Sb	1.5	0.00015
Al_2O_3	27.2	Ba	855	0.0855
Fe_2O_3	4.8	Be	0.1	0.00001
P_2O_5	0.1	Cd	0.5	0.00005
TiO_2	1.3	Cr	148	0.0148
CaO	6.4	Co	9	0.0009
MgO	1.0	Cu	47	0.0047
K_2O	0.5	Pb	91	0.0091
Na_2O	0.4	Mn	84	0.0084
SO_3	4.9	Mo	8	0.0008
	99.3	Hg	0.1	0.00001
		Ni	90	0.009
	East	As	0.5	0.00005
		Sn	15	0.0015
		V	115	0.0115
		Zn	172	0.0172
		Cl	150	0.015
		F	159	0.0159

35 bar cavity pressure

Coal flow of 31 000kg/hr,

58 000kg/hr 35%O2/air mixture and 1 500kg/hr steam

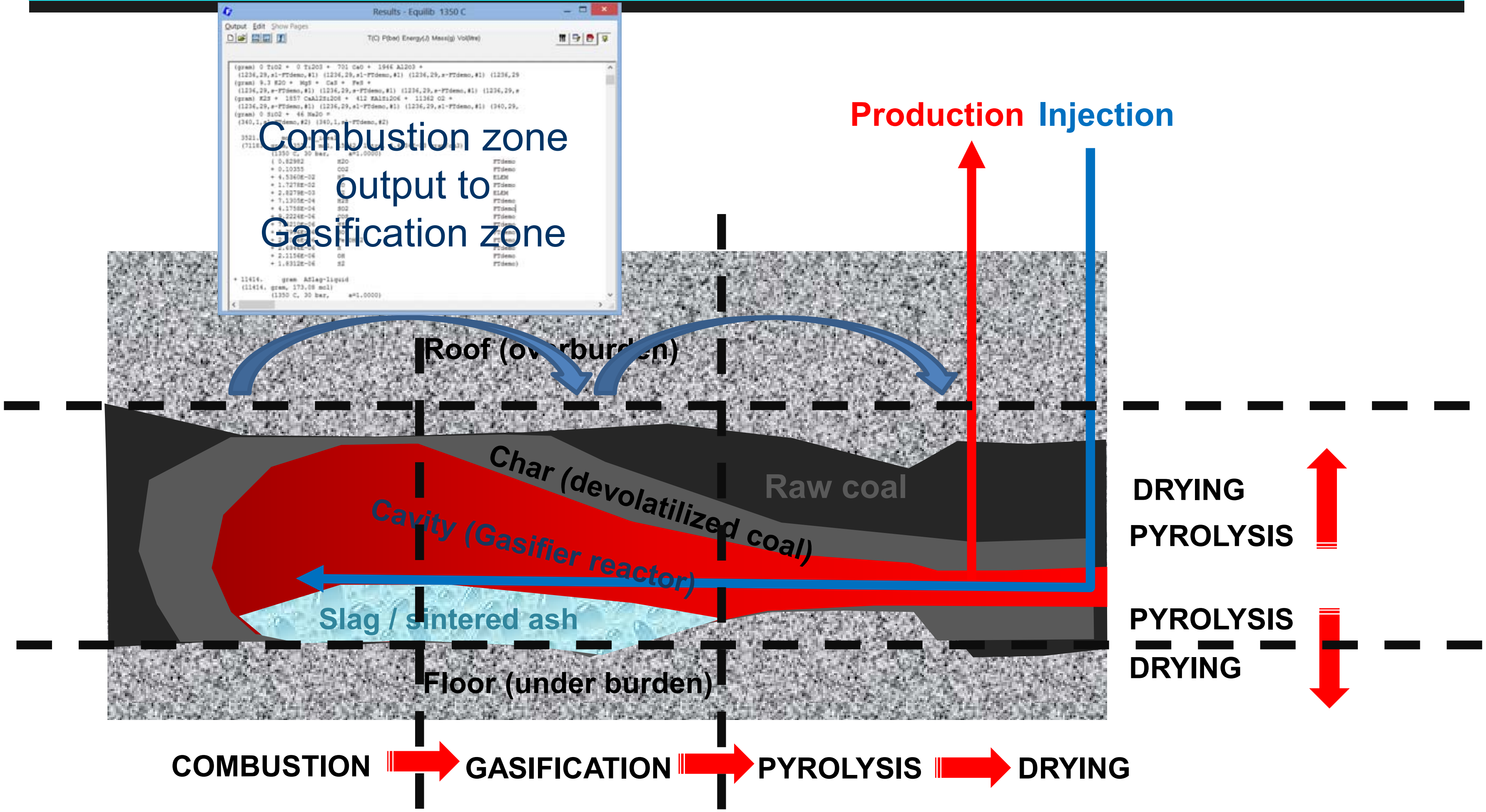
NO recycle of any stream

No contribution from roof and floor in this study – only as individual structure

18 trace elements included (Si-fuming and fouling not included).

Error on the data is in ^{o}C, which is ±25^{o}C.

Building a model for a FACTSAGE™ Equilibrium Simulation (cont.)



$C + ½ O_2 \rightarrow CO$

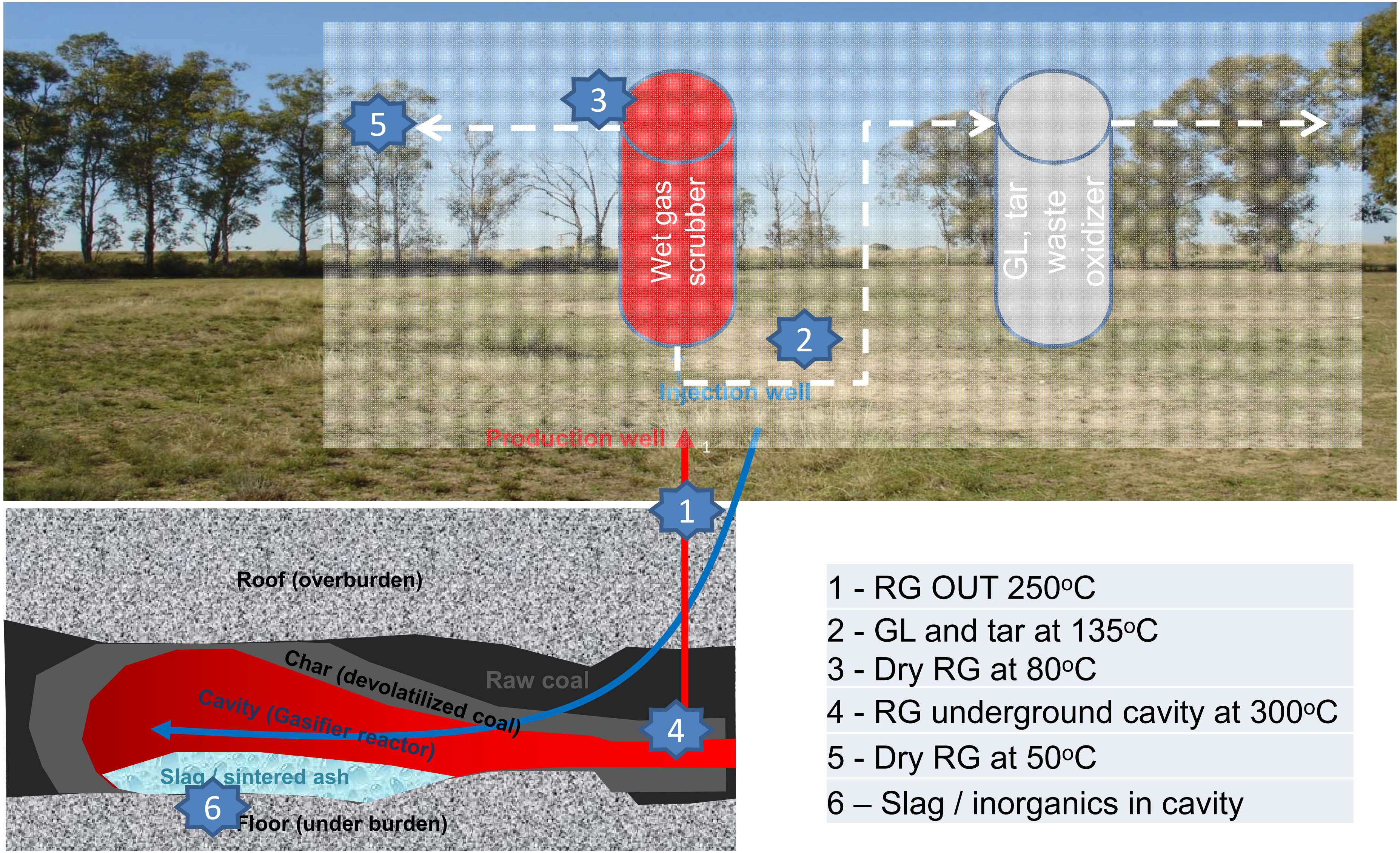
$C + O_2 \rightarrow CO_2$

$H_2 + O_2 \rightarrow H_2O$

$C + CO_2 \rightarrow 2\ CO$

$C + H_2O \rightarrow CO + H_2$

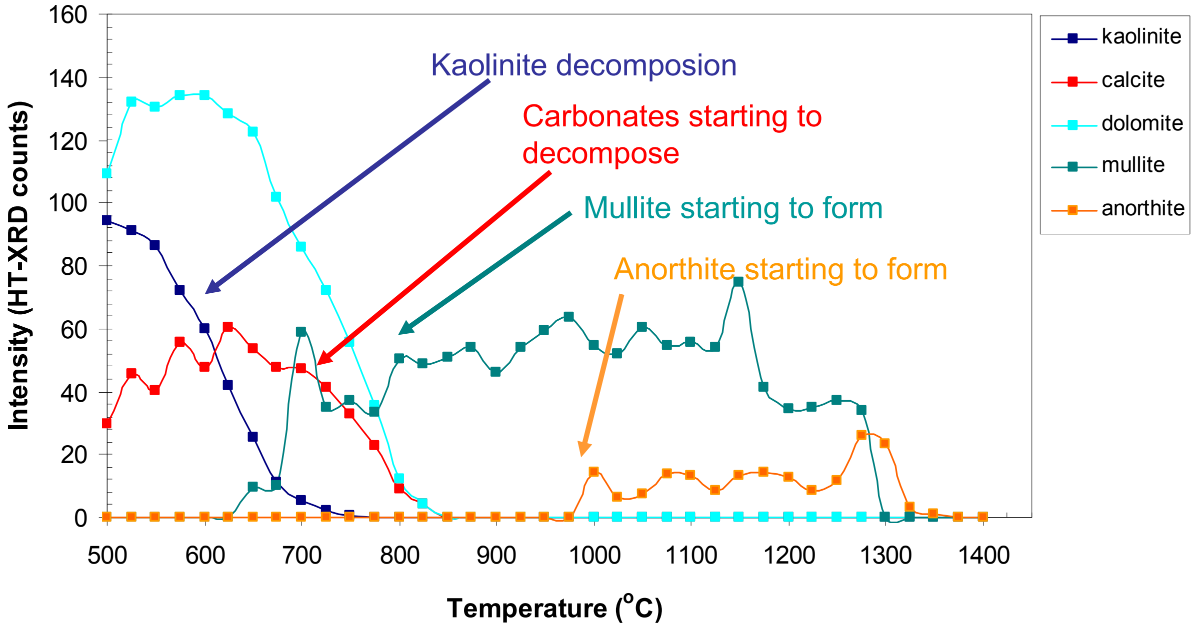
Building a model for a FACTSAGE™ Equilibrium Simulation (cont.)



1 - RG OUT 250°C
2 - GL and tar at 135°C
3 - Dry RG at 80°C
4 - RG underground cavity at 300°C
5 - Dry RG at 50°C
6 – Slag / inorganics in cavity

Mineral matter slag formation in the cavity
Input and output of mineral matter

Sample naming	Anatase	Dolomite	Halite (Sodium Chloride)	Kaolinite	Microcline	Muscovite	Plagioclase	Pyrite	Quartz	Rutile	Siderite
	(TiO_2)	($CaMg(CO_3)_2$)	(NaCl)	($Al_2(Si_2O_5)(OH)_4$)	($KAlSi_3O_8$)	(KAl3Si3O10 (OH)2)	((Na,Ca)(Si,Al)4O8)	(FeS2)	(SiO2)	(TiO2)	(FeCO3)
TUCG09/3 ROOF/1	0.7	0.7	0.61	17.48	12.47	5.20	16.12	0.47	45.17	1.12	0.00
TUCG09/3 /1	4.3	0.0	0.00	52.50	5.96	5.17	3.39	2.33	24.78	1.58	0.00
TUCG09/3 /2											
TUCG09/3 /3											
TUCG09/3 /4											
TUCG09/3 LOOR/1	1.3	0.9	0.07	37.74	9.08	8.75	1.96	0.39	38.60	1.14	0.11



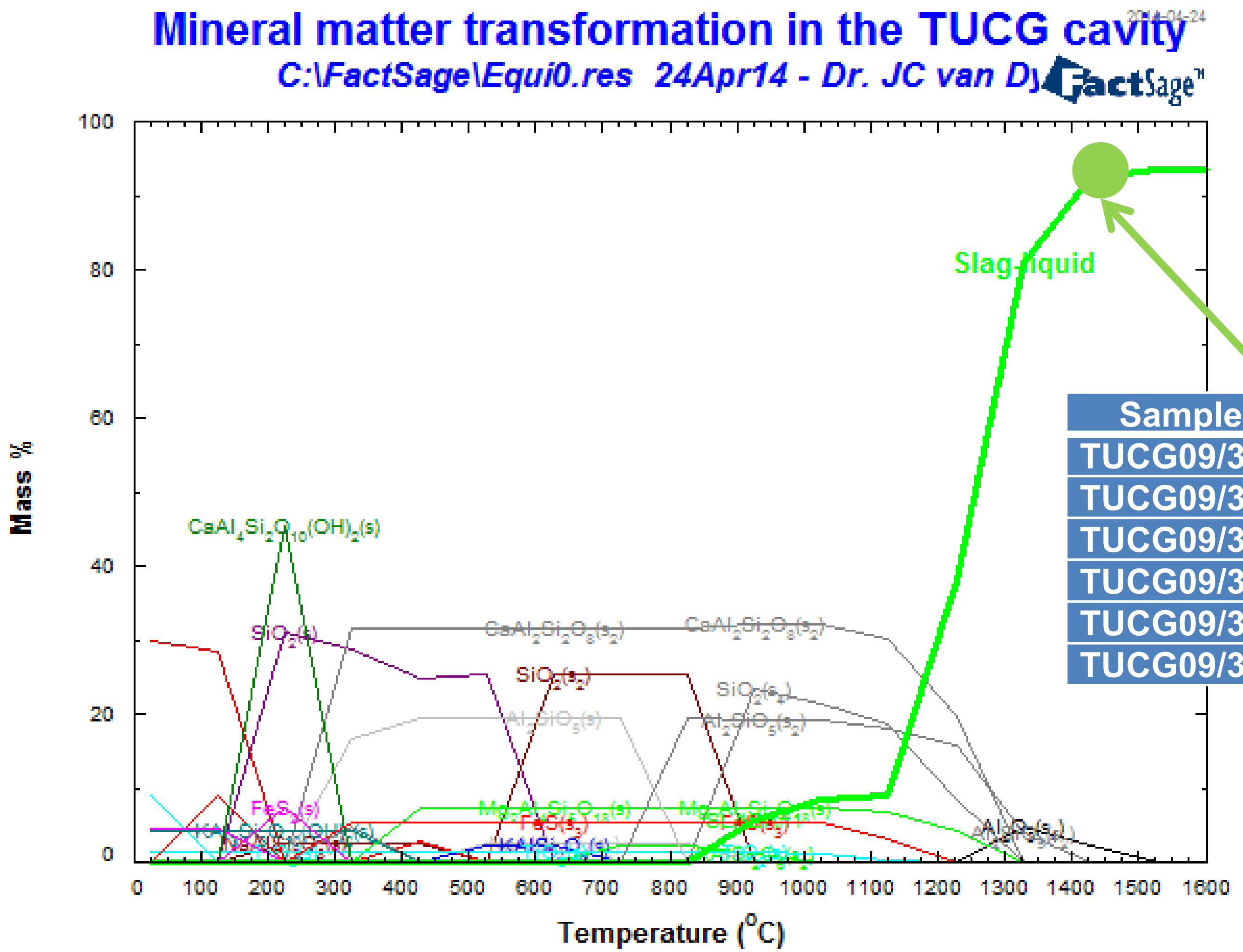
Kaolinite decomposion

Carbonates starting to decompose

Mullite starting to form

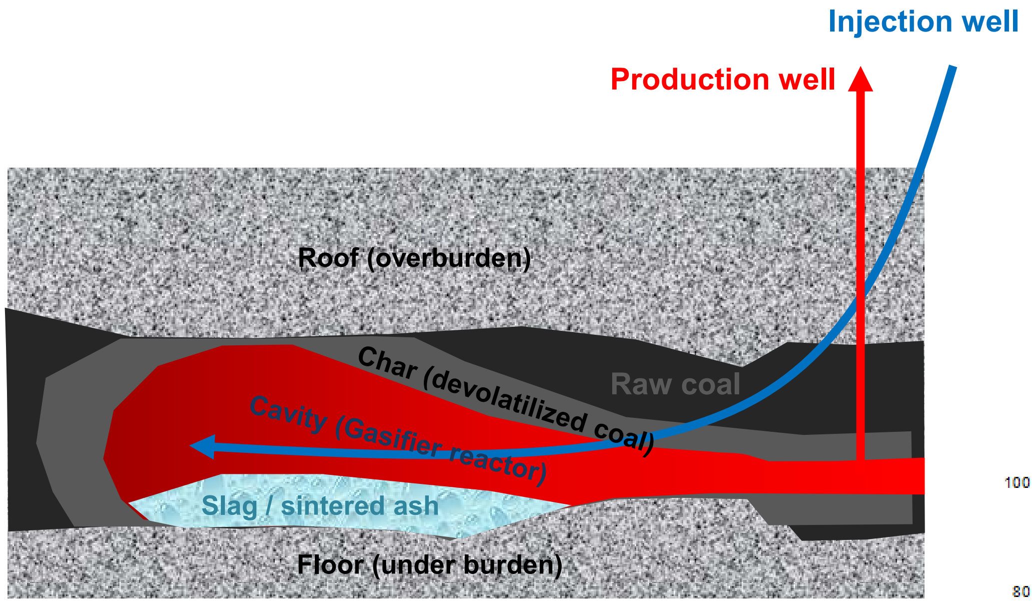
Anorthite starting to form

Mineral matter slag formation in the cavity
Mineral transformation in combustion zone

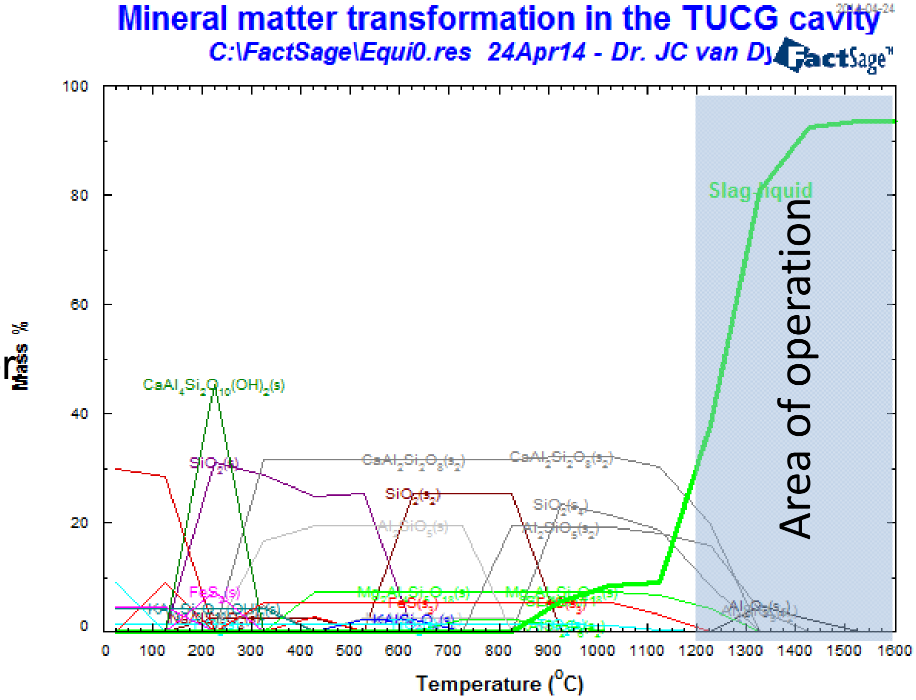


Sample naming	Flow T
TUCG09/3 ROOF/1	>1500
TUCG09/3 /1	>1500
TUCG09/3 /2	1430
TUCG09/3 /3	1420
TUCG09/3 /4	>1500
TUCG09/3 FLOOR/1	>1500

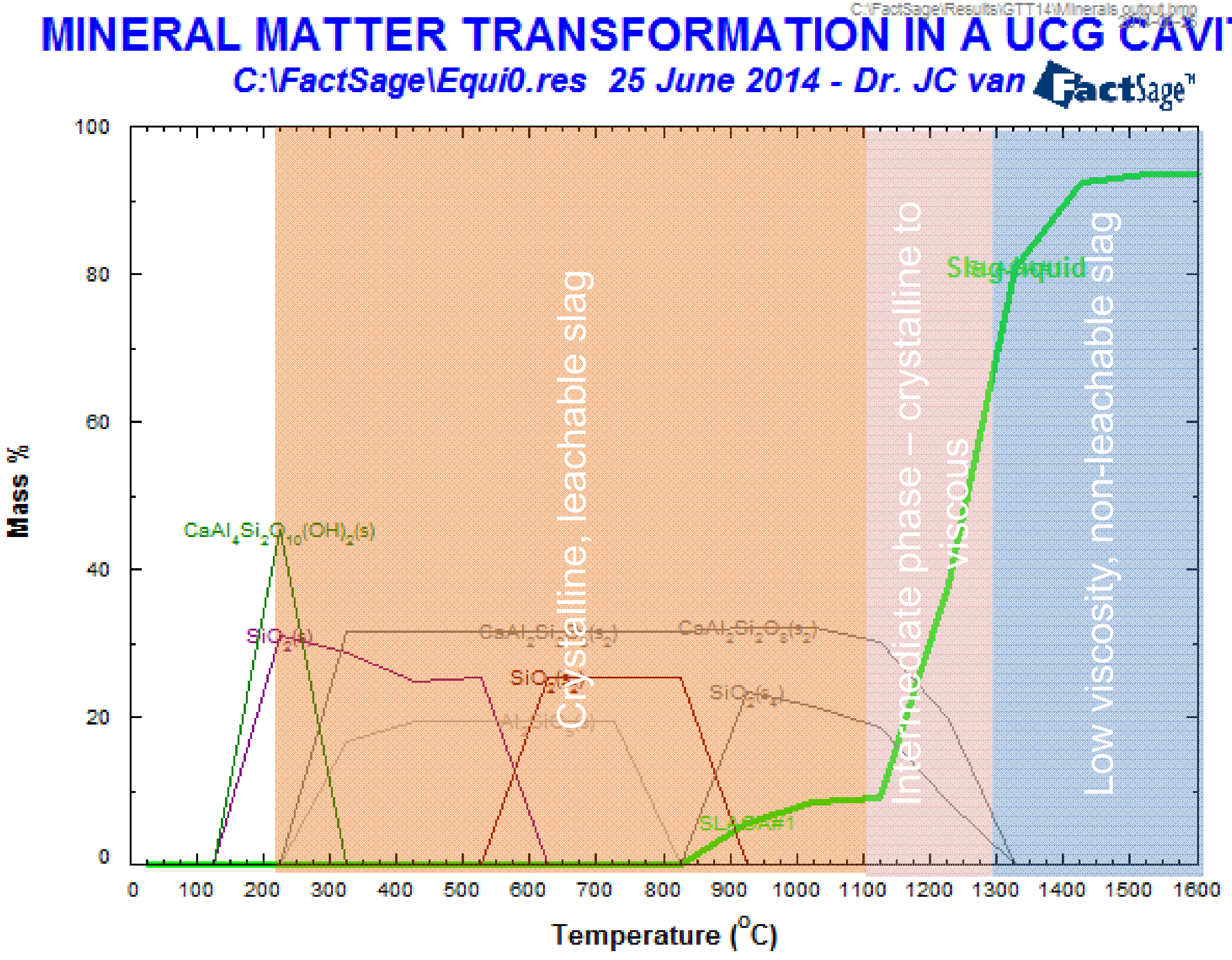
Mineral matter slag formation in the cavity
Mineral transformation in combustion zone



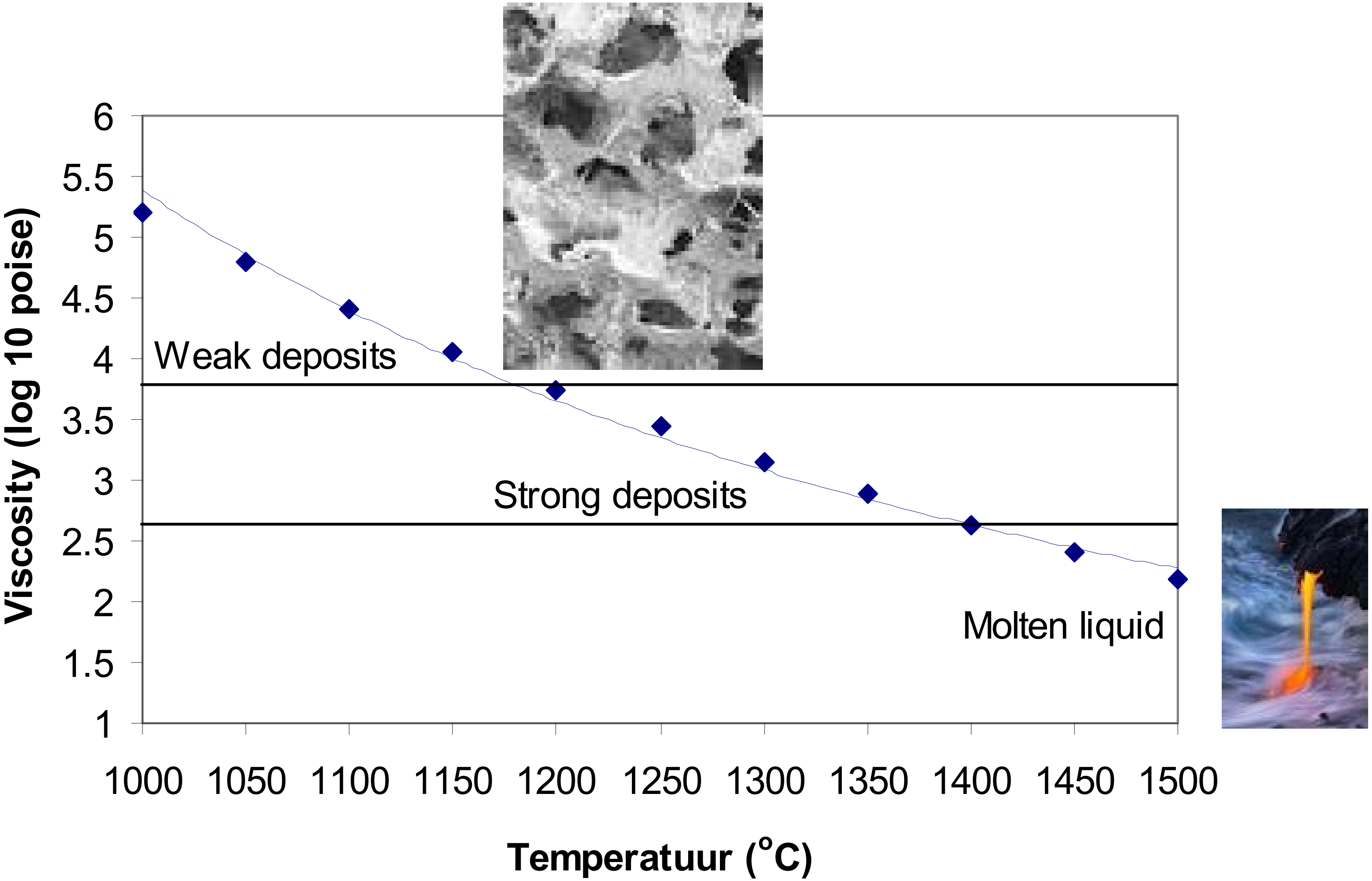
- Viscosity has to be low enough to flow to floor
- Mineral matter inherent / homogeneous
- High Si-containing slag, results in high temperature for easy flow



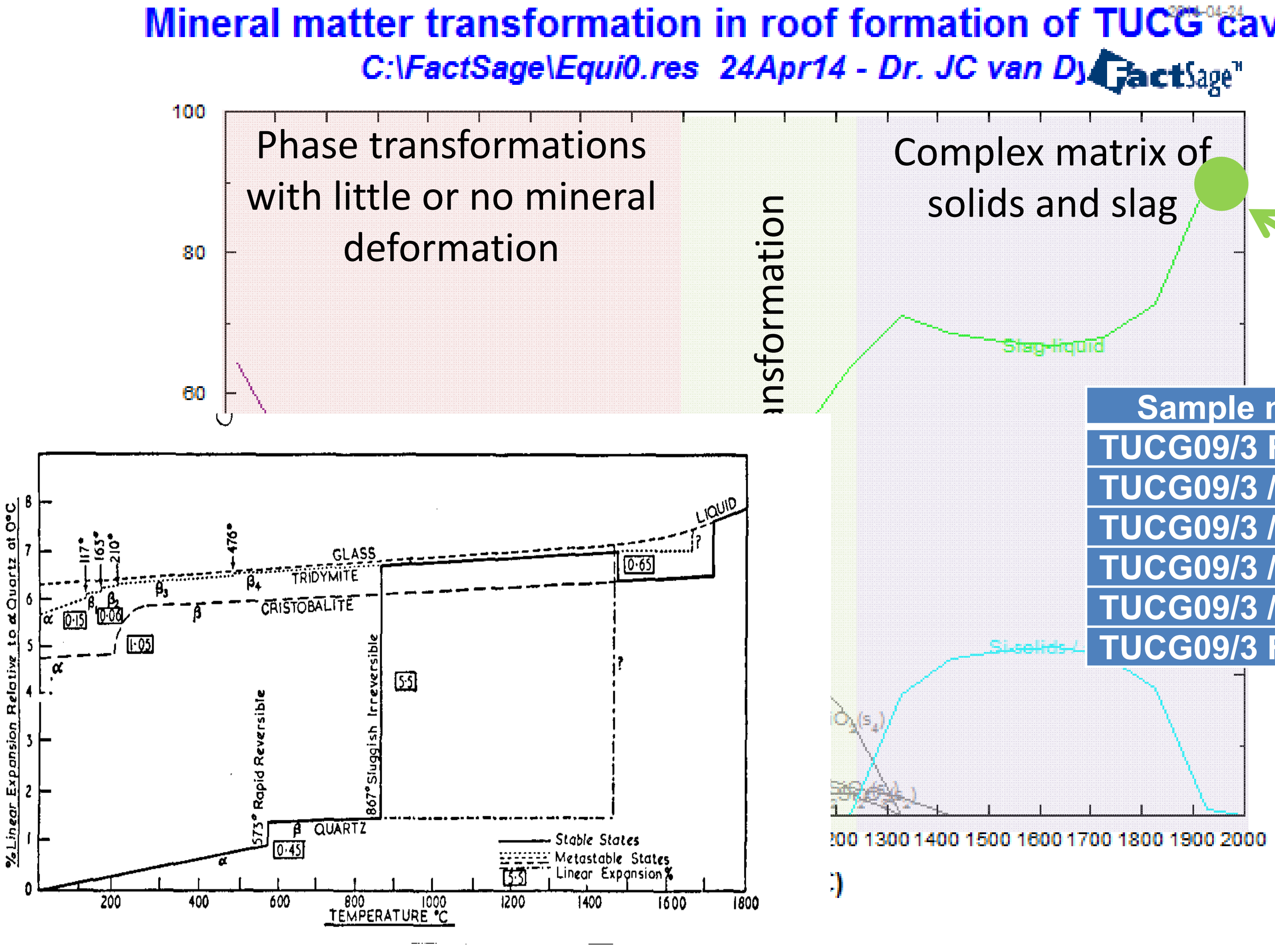
Mineral matter slag formation in the cavity
Crystalline versus slag - transformation



Mineral matter slag formation in the cavity
Crystalline versus slag - transformation



Mineral matter slag formation in the cavity Roof



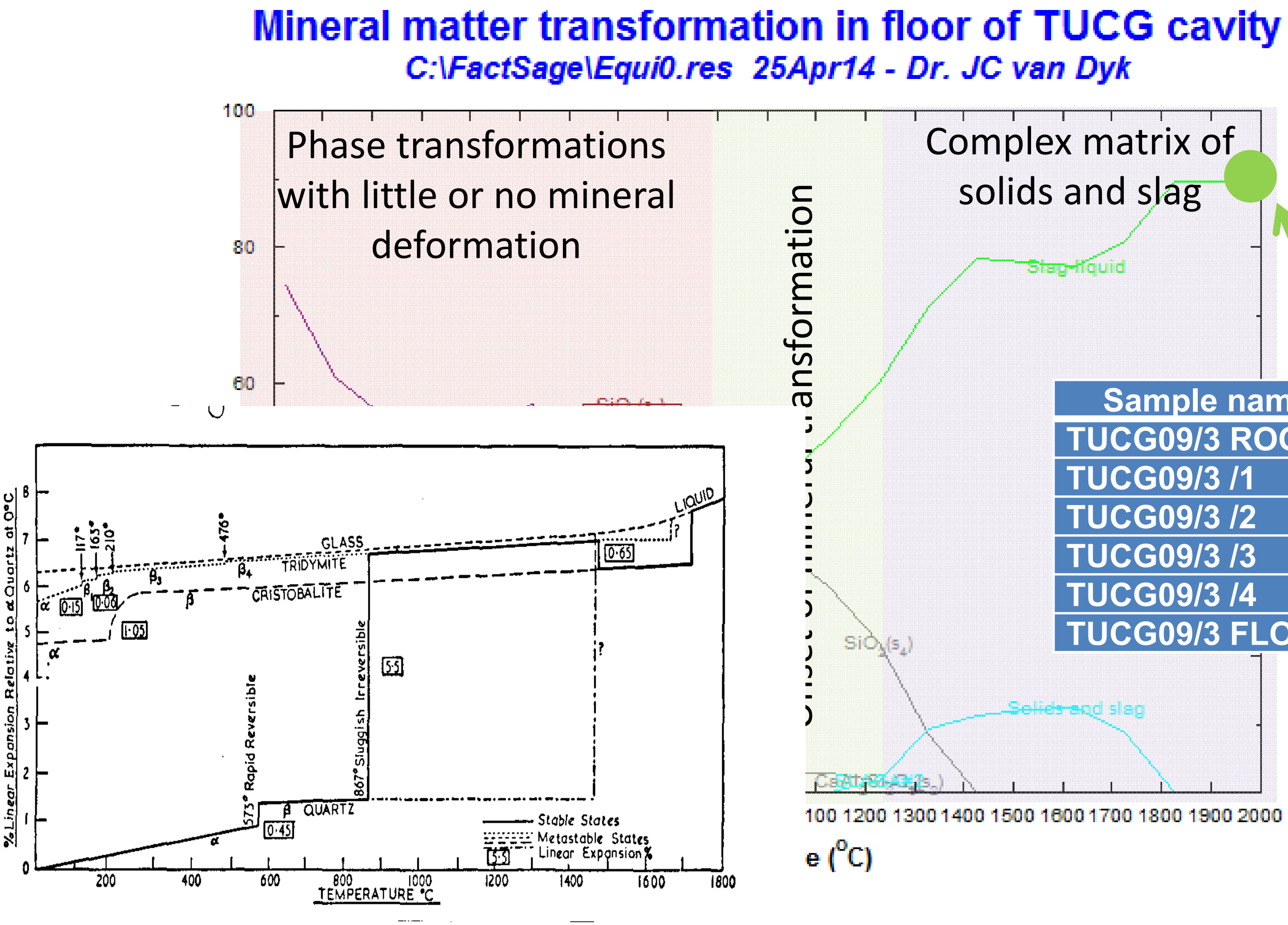
Phase transformations with little or no mineral deformation

nsformation

Complex matrix of solids and slag

Sample naming	Flow T
TUCG09/3 ROOF/1	>1500
TUCG09/3 /1	>1500
TUCG09/3 /2	1430
TUCG09/3 /3	1420
TUCG09/3 /4	>1500
TUCG09/3 FLOOR/1	>1500

Mineral matter slag formation in the cavity Floor



Mineral matter transformation in floor of TUCG cavity

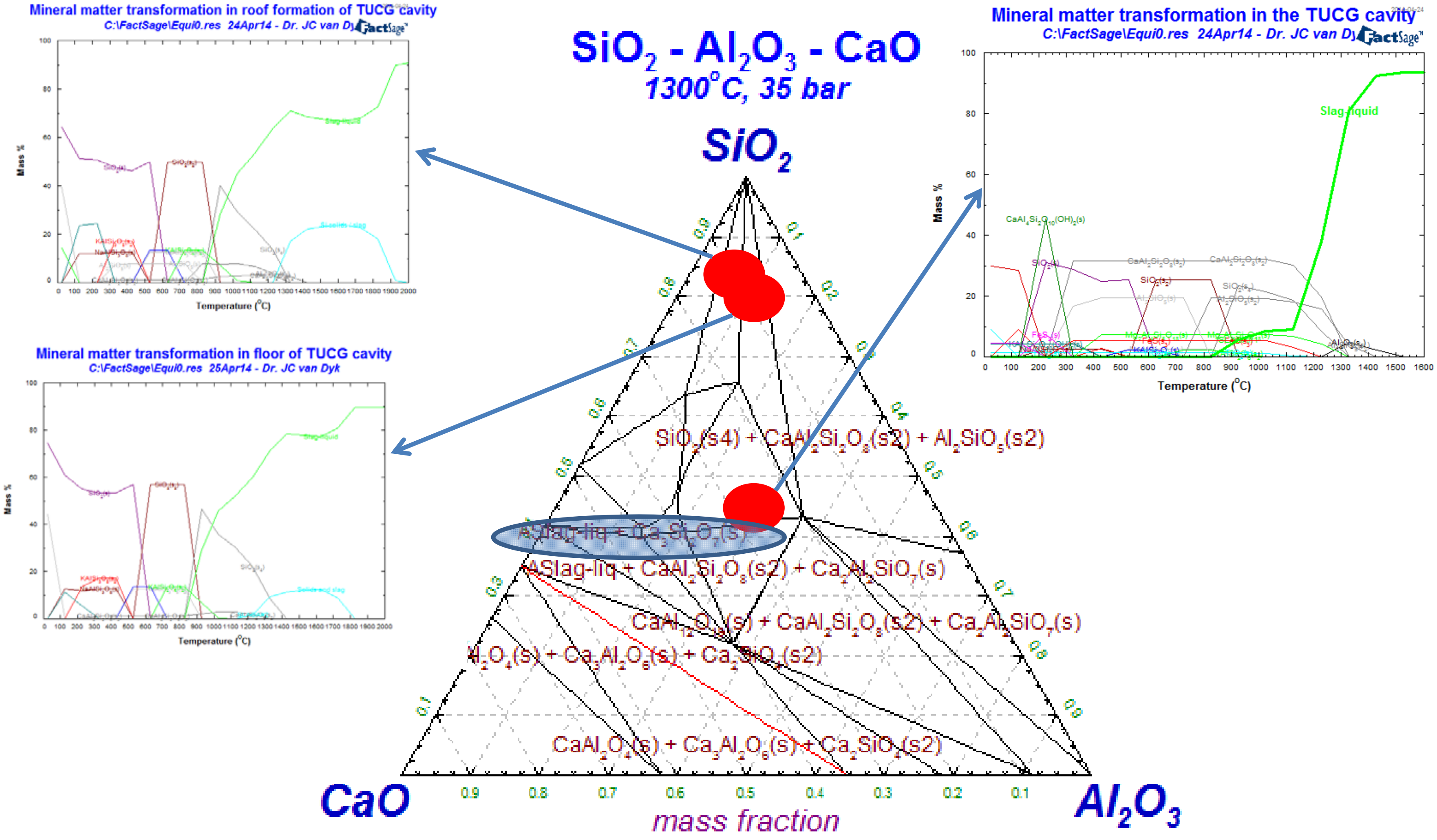
C:\FactSage\Equi0.res 25Apr14 - Dr. JC van Dyk

Phase transformations with little or no mineral deformation

Complex matrix of solids and slag

Sample naming	Flow T
TUCG09/3 ROOF/1	>1500
TUCG09/3 /1	>1500
TUCG09/3 /2	1430
TUCG09/3 /3	1420
TUCG09/3 /4	>1500
TUCG09/3 FLOOR/1	>1500

Mineral matter slag formation in the cavity
Coal versus roof and floor



Mineral matter transformation in roof formation of TUCG cavity

C:\FactSage\Equi0.res 24Apr14 - Dr. JC van Dy

Mineral matter transformation in floor of TUCG cavity

C:\FactSage\Equi0.res 25Apr14 - Dr. JC van Dyk

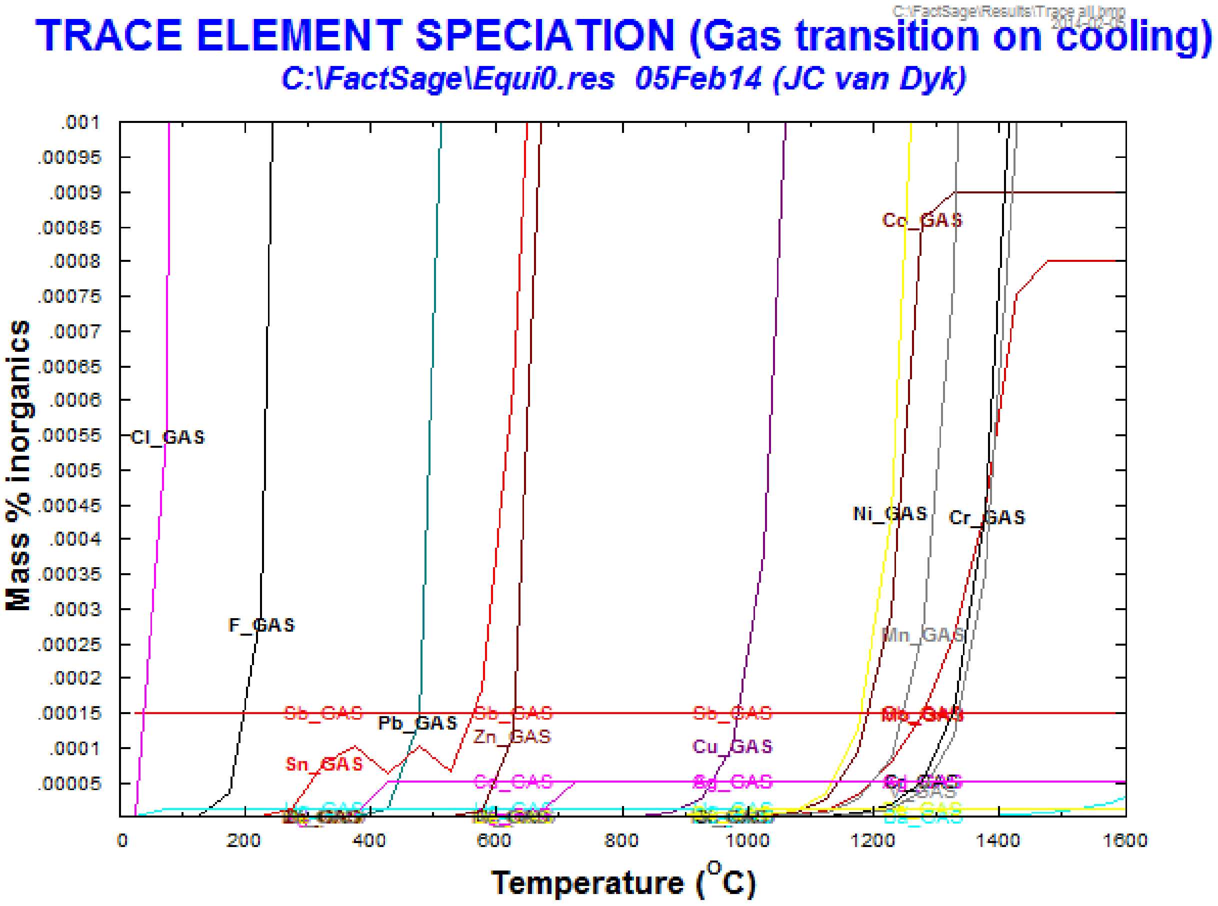
Mineral matter transformation in the TUCG cavity

C:\FactSage\Equi0.res 24Apr14 - Dr. JC van Dy

SiO_2 - Al_2O_3 - CaO

1300°C, 35 bar

Trace element speciation – from 350m underground to surface treatment

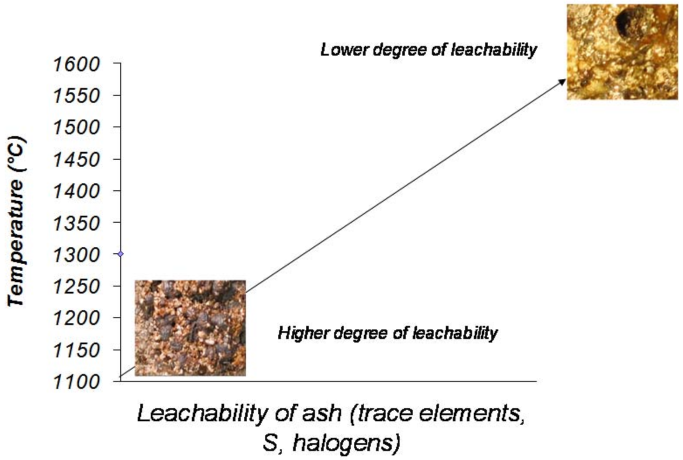


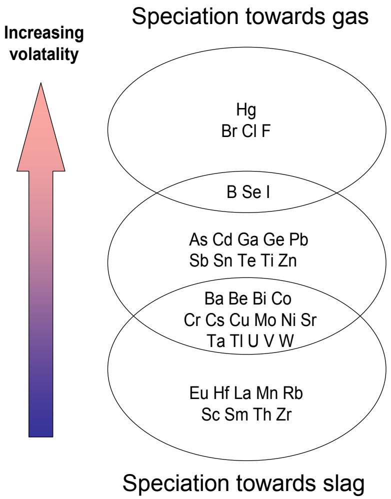
TRACE ELEMENT SPECIATION (Gas transition on cooling)

C:\FactSage\Equi0.res 05Feb14 (JC van Dyk)

Trace element speciation – from 350m underground to surface treatment

mg/hr	Si	Al	Fe	P	Ti	Ca	Mg	K	Na
1 - Stream 2101 RG OUT 250	9.68791E-33	2.3318E-30	3.9809E-08	3.7464E-25	3.3692E-39	9.3736E-23	3.0269E-17	1.0296E-12	1.7492E-14
2 - GL and tar at 135	0	-6.2888E-59	2.2185E-06	-2.1575E-53	0	-2.7939E-44	-2.5694E-36	-1.7283E-28	-4.397E-30
3 - Dry RG at 80	8.25733E-55	9.7359E-49	3.1277E-17	3.1836E-45	4.4996E-62	6.3548E-36	1.857E-29	7.8707E-24	1.1467E-25
4 - RG underground cavity at 300	6.93976E-28	2.1161E-26	2.255E-06	1.323E-20	3.8841E-34	6.37E-20	8.1869E-15	1.8524E-10	4.078E-12
5 - Dry RG at 50	0	6.2888E-59	2.2629E-23	2.1575E-53	0	2.7939E-44	2.5694E-36	1.7283E-28	4.397E-30
In cavity or ash matrix	7636513573	4462730338	1040752973	13529289.9	241537607	1417956595	192551273	133820216	68993368.7





Increasing volatility

Speciation towards gas

Hg
Br Cl F

B Se I

As Cd Ga Ge Pb
Sb Sn Te Ti Zn

Ba Be Bi Co
Cr Cs Cu Mo Ni Sr
Ta Tl U V W

Eu Hf La Mn Rb
Sc Sm Th Zr

Speciation towards slag

Franklin. R. N., R. P. Jensen and R. 1. Perry, "SCGP - Efficient Clean Coal Power for Today and Tomorrow," EPRI Conference on Technologies for Producing Electricity in the Twenty-First Century, October 30 - November 2, 1989.

Volatility of trace components

	CORUS TEST RESULTS			FACTSAGE (EQUILIBRIUM SIMULATION) - % in slag	* Shell, 1990, Perry, et. al.		
	COAL	SLAG (avg of 13)			COAL	SLAG	
	mg/kg	mg/kg	% in slag versus coal feed with 28% ash		mg/kg	mg/kg	% in slag versus coal feed with <10% ash
Hg	ND	ND	ND	0	0.13	0.27	16.5
Br	ND	ND	ND	0	1	1	7.9
Cl	ND	ND	ND	0	500	500	8
F	ND	ND	ND	0	152	129	6.8
B	ND	ND	ND	0	55	1100	159
As	0.71	0.404	14.9	30	4.4	87	157
Zn	9.4	13.7	38	0	9.3	68	58
Pb	1.9	2.987	41.2	0	2.31	0.38	1.3
Cd	0.227	0.509	58	0	0.1	0.08	6.3
Se	0.33	0.718	57	2	0.31	2.4	61.7
Ni	34.52	71.9	54	100	8.5	1400	1313
Ba	311	791	66	100	134	954	56
Co	2.45	5.8	62	100	2.8	195	555
Cu	13.6	41.9	80.7	94	7.8	212	216
Mo	0.48	2.44	133	100	0.77	17.36	179
V	28.06	194	181	100	11.85	187	125
Cr	23.06	123	140	100	1.9	172	722
Mn	80.85	232	75	100	190	372	15

In summary

- The behaviour, and importantly the mineral matter composition of a coal source, directly relates to the ash fusion temperature (AFT) profile, trace element speciation and mineral transformations of the coal source.

- Factsage^{TM} can assist to assess coal ash fusibility, leachability and melting characteristics and it is furthermore used to predict the melting behaviour of the coal ash in coal conversion processes.

- It has been demonstrated and published before that the ash flow temperature can be correlated with equilibrium calculations, and that such equilibrium calculations provide useful information regarding the phase transitions that take place in a UCG cavity.

- Previous studies have confirmed that the slag-liquid flow temperature simulations for coal and individual mineral types compared favourably with the actual measured ash flow temperature and are within the experimental error of an AFT analysis (±30^{o}C).

References

1. Alpern, B., Nahuys, J., Martinez, L., Mineral matter in ash and non-washable coals – Its influence on chemical properties, In Symposium on Gondwana Coals, Lisbon – proceedings and papers, vol. 70 1984, p299-317
2. Comun. Serv. Geol. Portugal, 1984, t. 70, fasc. 2, pp. 299-317, 1988.
3. Bale, C.W., Chartrand, P., Degterov, S.A., Eriksson, G., Hack, K., Manfoud, R. B., Melancon, J., Pelton, A.D. and Peterson, S., FactSage Thermochemical Software and Databses, GTT-Technologies, Germany, Calphad, 2002, 26, p. 189-228.
4. Collet, A.G., Matching gasifiers to coal, IEA Clean Coal Centre, 2002, p.1-64.
5. Gray, V.R., Prediction of ash fusion temperature from ash composition for some New Zealand coals, Fuel 66 (1987), p.1230-1239.
6. Higman, C. and Van der Burgt, M., Gasification, Gulf Professional Publishing, Amsterdam, 2007.
7. Holt, N. Gasification technology status – December 2006, Electric Power Research Institute, Palo Alto, 2006
8. IEA Clean Coal Centre, Coal quality assessment – the validity of empirical tests, September 2002.
9. Jak, E. and Hayes, P.C., Applications of the new F*A*C*T database to the prediction of melting behaviour of coal mineral matter, Coorperative Research Centre for Black Coal Utilisation, Pyrometallurgy Research Group, The University of Queensland, Australia, p.1-9, 2002.
10. Jak, E., Prediction of coal ash fusion temperatures with the FACT thermodynamic computor package, Fuel, 81, 2002, p. 1655-1668.
11. Keyser, M.J., Personal communication, Sasol Technology, martin.keyser@sasol.com, 2006.
12. Keyser, M.J., van Dyk, J.C., 17th International Pittsburgh Coal Conference, 2000, Pittsburgh, USA, Full Scale Sasol/Lurgi Fixed Bed Test Gasifier Project: Experimental Design and Test Results.
13. Keyser, M.J., van Dyk, J.C., Coetzer, R.L.C., Wagner, N.J., 8th Coal Science and Technology Conference of the Fossil Fuel Foundation of Africa, South Africa, 15-17 October 2002, Full Scale Sasol/Lurgi Fixed Bed Test Gasifier Project: Impact of particle size distribution, destoning and gasifier operating conditions on sulphur production.
14. MICROBEAM TECHNOLOGIES, INC., www.microbeam.com, 2003.
15. Ross, D.P., Kosminski, A. and Agnew, J.B., Reactions between sodium and silicon minerals during gasification of low-rank coal, 12th International Conference on Coal Science, 2003, Australia, p. 1-9.
16. Seggiani, M., Empirical correlations of the ash fusion temperatures and temperature of critical viscosity for coal and biomass ashes, Fuel 78 1999, p. 1121-1125.
17. Slegeir, W.A., Singletary, J.H. and Kohut, J.F., Application of a microcomputor to the determination of coal ash fusibility characteristics, Journal of Coal Quality, 1988, Volume 7, Number 2, p. 48-54.
18. Van Dyk, J.C., Keyser, M.J., van Zyl, J.W., Suitability of feedstocks for the Sasol-Lurgi Fixed Bed Dry Bottom Gasification Process, GTC Conference, San Francisco, USA, October 2001.
19. Van Dyk, J.C., Melzer, S. and Sobiecki, A., Mineral matter transformations during Sasol-Lurgi fixed bed dry bottom gasification – utilization of HT-XRD and FactSage modelling, Minerals Engineering 19 (2006), 1126-1135.
20. Van Dyk, J.C., PhD Thesis – Manipulation of gasification coal feed in order to increase the ash fusion temperature of the coal to operate the gasifiers at higher temperatures, North West University, 2006.
21. Van Dyk, J.C., Waanders, F.B. and van Heerden, J.H.P. Quantification of oxygen capture in mineral matter during gasification, Fuel 87, 2008, p2735-2744.