Corrosion of High Alumina Castables by Liquid Ashes during the Gasification of Sewage Sludge

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The overall objective of this work is to understand the thermo chemical interactions between different high alumina refractory materials and slag during the gasification of biomass (sewage sludge).
The slag behaviour and the corrosion between different high alumina-based castables and the liquid ashes are studied. Corrosion tests were carried out using static and dynamic tests. The loss of thickness of the initial interface was used to evaluate the amount of corrosion and impregnation, whereas the dynamic test was performed out in order to quantify the erosion phenomenon. Quantitative and qualitative analysis were carried out using SEM and DRX. These techniques were also used to determine the liquidus temperature of sewage sludge ashes after quench at high temperature.
Results shows the presence iron oxide, lime, and iron/lime phosphate crystals ($Ca_9Fe(PO_4)_7$). The liquidus temperature of slag is located between 1250 °C and 1300 °C.
Trials of corrosion indicate a higher impregnation and corrosion for rich alumina castables (tabular/alumina and alumina/spinel).
Chrome alumina refractory presents a very limited corrosion and andalusite-based refractory exhibits limited penetration.

1 Introduction

This paper deals with the selection of refractory materials for the gasification of dried sewage sludge in an entrained flow reactor in order to produce a "syngas" (CO, H_2) at 1400 °C. This "syngas" can be used to produce electricity (through a gas turbine) or can be transformed in biofuel using Fisher Troppsch process. The high organic content of sludge (50 to 70 mass-% of total dry solids) constitutes an interesting potential renewable energy resource [1]. Moreover, producing energy by means of sludge reduces the quantity of waste.

Gasification of sewage sludge requires innovative refractory technologies due to the particularly high inorganic content of this biomass (30 to 50 mass-% of the dry solids are composed of mineral matter: SiO_2, Al_2O_3, Fe_2O_3, CaO, P_2O_5, K_2O, Na_2O).

It is well known that, during gasification, aggressive molten mineral matters (mainly ashes) will soften, liquefy and deposit on the refractory lining of the reactor. Moreover, the presence of P_2O_5, K_2O, Na_2O oxides in the sludge mineral matter promotes the formation of liquid ashes with a very low liquidus temperature. These molten ashes corrode both the refractory lining and the metallic structure in the gasification reactor. They also have an effect on the working temperature of the entrained flow reactor. Nevertheless P_2O_5, K_2O and Na_2O species are known to be volatile at high temperatures and then may increase the temperature liquidus of the molten ashes.

The behaviour of a complex system such as sludge ashes at high temperature is still poorly understood [2–5]. Therefore, it is essential to understand the effect of these inorganics on the wear of the refractories during gasification in an entrained flow reactor.

The overall aim of this work is:

- to study the thermo-chemical properties of sludge mineral matter at high temperature and to understand the interactions between different refractory materials and inorganic species under entrained-flow gasification conditions
- to offer a solution to increase the lifetime of the refractory lining.

The behaviour of P_2O_5, largely present in the sludge, will be particularly studied and different refractories, such as andalusite/fireclay/corundum, bauxite, tabular alumina,

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Tab. 1 Composition (mass-%) of sludge ashes A1 (intermediate) and A2 (high P_2O_5 content)

Composition/Ashes	A1	A2
SiO_2	36,4	21,2
CaO	15,8	23,9
Fe_2O_3	14,3	17,7
Al_2O_3	15,2	12,4
P_2O_5	16,4	22,4
Na_2O	0,5	1,9
K_2O	1,5	0,3

Tab. 2 Liquidus temperatures and primary crystallization for A1 and A2 sludge ashes

	T Liquidus [°C]	
Sludge ashes	**A1**	**A2**
Quench/SEM	1280–1300	1325–1350
HTDRX	1287–1319	1315–1350
Quench/DRX	1250–1267	1360–1380
Primary crystallization	$Ca_9Fe(PO_4)_7$	$Ca_9Fe(PO_4)_7$

chrome-alumina and spinel alumina castables will be evaluated.

2 Experimental procedure

The chemical compositions of two different ashes, A1 and A2, containing mainly five oxides SiO_2, Al_2O3, Fe_2O_3, CaO and P_2O_5 were studied using X-ray fluorescence.

Complementary characterization techniques such as high temperature X-ray diffraction, SEM analysis after quench in sealed Pt were also used to determine the temperature of liquidus of these ashes.

Thermo gravimetric analysis (TGA) measurements were carried out in order to determine the behaviour of the phosphorus during the thermal treatment. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to determine the liquidus temperature of both sludges [6–7].

The corrosion by the liquid ashes of different castables was studied on the laboratory scale (static and dynamic trials) [9].

The main purpose of these tests is to find out and establish the existing relationships between:

- the impregnation and the transport of slag
- the phase changes and the resulting modifications in the refractory properties [9–10].

Three different trials were performed:

- A static corrosion at 1500 °C, during 5 h, with A1 ashes as aggressive agent. A thermal cycle was realized according to the following steps:
  – Annealing at 1500 °C
  – Temperature was then stabilized at a plateau of 1500 °C for 5 h
  – The crucible was quenched at the end of step (b) to avoid the crystallization during cooling.
- A comparative static corrosion test (1400 °C, during 5 h, under oxidizing and reducing atmosphere respectively, with A1 ashes as aggressive agent) was carried out to evaluate the effect of the reducing atmosphere (mixture of $H_2/CO/N_2$) on the corrosion of castable.
- A dynamic corrosion test (1500 °C, during 12 h, with A1 ashes as aggressive agent) was performed to observe the erosion phenomenon and to simulate the real conditions of the gasification.

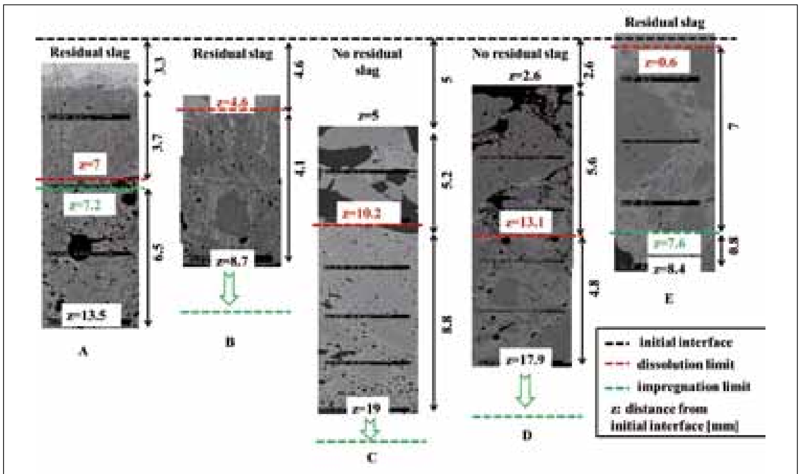

Fig. 1 SEM (bse mode) microstructures of corroded area after isothermal test at 1500 °C during 5 h

3 Results

3.1 Slag behaviour

A1 is an average composition of 34 different sewage sludge ashes [11] whereas A2 contains the highest percentage of P_2O_5 (Tab. 1).

The different liquidus temperature measurements of the two typical sludge ashes are summarized in Tab. 2. The results are quite consistent. The liquidus temperature are located between 1250 °C (determined by XRD) and 1300 °C (SEM) for A1 sludge and between 1350 °C (SEM) and 1380 °C (XRD) for A2 sludge. X-ray diffraction show the presence of Fe_2O_3, lime and iron/lime phosphate crys-tals ($Ca_9Fe(PO_4)_7$) at high temperature. $Ca_9Fe(PO_4)_7$ is the primary crystalline phase for both sludge ashes. Results show that the temperature of the liquidus increases with the amount of P_2O_5 and CaO. TGA measurements show a loss of weight at T <900 °C. This is due to decarbonisation of $CaCO_3$ and the decomposition of P_2O_5 precursor according to Bougel and al [12]. No weight loss was observed at temperature higher than 900 °C.

3.2 Corrosion tests

Five different refractories were tested. Main aggregates are respectively of andalusite (A), bauxite (B), tabular alumina (C), spinel alumina (D) and chrome alumina (E).

The microstructures of corroded castables are presented in Fig 1. The different castables are deeply penetrated by slag, except andalusite based refractory (A) which exhibits limited penetration. Chrome alumina (E) refractory presents a very limited corrosion. The high alumina castables (tabular alumina and spinel alumina) are deeply impregnated and corroded.
Bauxite and andalusite castables seem to be more corroded under reducing atmosphere.
Fig. 2 shows the results for dynamic trial. The most resistant material is the chrome alumina refractory (E) (only 1 % of initial thickness was dissolved). Andalusite (A), bauxite (B), and tabular alumina (C) castables present a loss of thickness of respectively of 12,3 %, 10,1 % and 14,3 % respectively. Spinel alumina refractory (D) has a very poor resistance to erosion. In fact, 90 % of the initial thickness is dissolved by slag.
SEM observations (Fig. 3) of the post-mortem andalusite based refractory show a zone of slag adjacent to a zone of precipitated solid phases. A mineral layer of mullite with well-defined boundaries is observed.

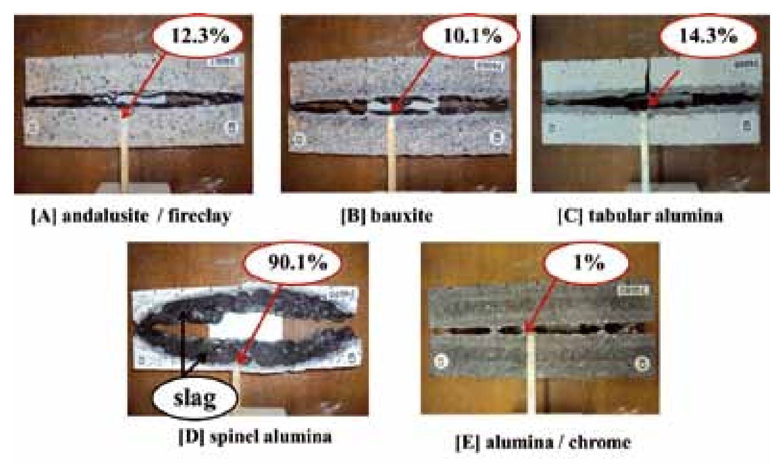

Fig. 2 Key brick after dynamic corrosion test

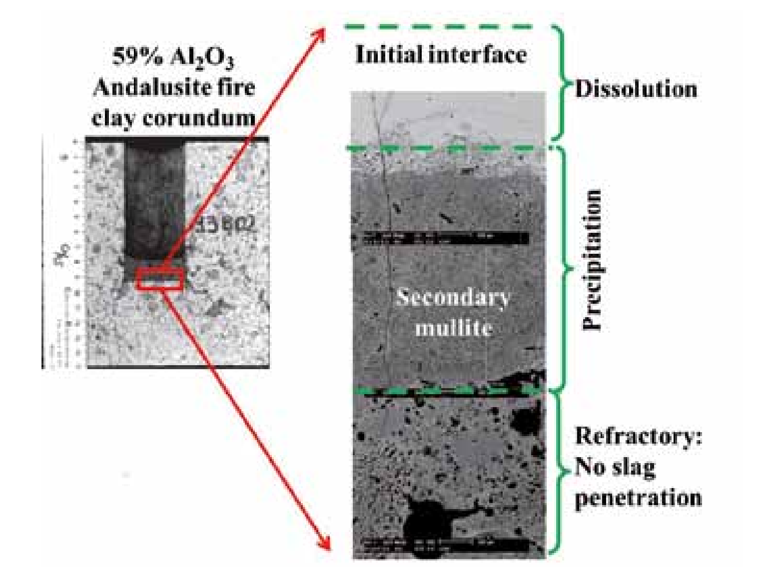

Fig. 3 SEM microstructure (back scattered electron) of final corrosion interface for andalusite/fireclay castable

4 Discussion

4.1 Slag behaviour

The experimental results obtained with XRD and SEM/EDX analysis such as the liquidus temperature, the primary crystallization has ($Ca_9Fe(PO_4)_7$) and the formation of solid phases as a function of temperature are in accordance.
The increase in the temperature of liquidus is due to a larger amount of $Ca_9Fe(PO_4)_7$ primary crystals in A2 slag. The association of phosphorus with calcium and iron oxides limits the volatilization of P. The liquidus temperatures of slags are in the range of the working temperatures of the entrained flow reactor (currently between 1300 °C and 1500 °C).

4.2 Corrosion tests

Tab. 3 presents the main results of this study. These results clearly show that the viscosity of the liquid phases strongly affects the corrosion behaviour of high-alumina refractories in a gasification reactor for sewage sludge. They indicate a higher impregnation and a higher corrosion for high alumina

Tab. 3 Sum up of trials of corrosion

	Refractory	A Andalusite, Fireclay, Corundum		B Bauxite		C Tabular Alumina		D Spinel Alumina		E Chrome Alumina	
Corrosion Test	Mineralogy	Mullite Anorthite Corundum		Mullite Corindon Corundum		Corindon Anorthite Corundum		Corundum Spinel Hibonite		Corundum SS Al_2O_3–Cr_2O_3 Hibonite	
		cor.	imp.	cor.	imp.	cor.	imp.	cor.	imp.	cor.	imp.
Static	1500 °C 5 h oxidizing atmosphere	*	Ø	*	**	***	***	**	**	Ø	**
	1400 °C 5 h reducing atmosphere	=	=	=	+	=	=	=	=	=	=
Dynamic	1500 °C 12 h 30	=	=	=	–	=	–	+++	–	=	–

castables (tabular alumina). The weak penetration of slag in the andalusite/fireclay/corundum refractory can be explained by the formation of a protective layer of mullite at the slag-refractory interface. The spinel alumina castable is completely destroyed during the dynamic corrosion trial. This is due to the dissolution of two phases in the slag (hibonite: $CaAl_{12}O_{19}$ and spinel alumina: Al_2MgO_4). The formation of a thin layer of chrome alumina solid solution limits the dissolution rate of castable at the interface.

5 Conclusion

The liquidus temperatures of two sludge ashes were determined using SEM and X-ray diffraction techniques. The results indicate the formation of a primary lime and iron/lime phosphate crystalline phase which disappears at 1300 °C ± 20 °C (slag A1) and 1350 °C ± 20 °C (slag A2). A high content of lime and P_2O_5 in slag A2 is responsible of a higher liquidus temperature.

Static and dynamic corrosion tests show that andalusite/fireclay/corundum and alumina chrome castables are less corroded.

Chromium oxide based refractories are today the best material solution to resist to the corrosion conditions in biomass gasification reactors. Unfortunately, under certain working conditions, chromium oxide can oxidize to hexavalent chromate which is very toxic and undesirable with respect to the environment as well as health and safety.

For this innovative application, a mullite/ zircon refractory may be well adapted and will be developed in the future. The presence of zirconia decreases the dissolution rate of refractory whereas the in situ formation of mullite avoids the slag impregnation and increases the lifetime of refractory lining.

References

[1] Dupont, C.; et. al.: Biomass pyrolysis experiments in an analytical entrained flow reactor between 1073 K and 1273 K. Fuel **87** (2008) [7] 1155–1164

[2] Watson, E.B.: Two-liquid partition coefficients: experimental data and geochemical implications. Contributions to Mineralogy and Petrology **56** (1976) [1] 119–134

[3] Dickey jr., J.S.; et al.: Geochemistry and petrology of dredged basalts from the Bouvet triple junction, South Atlantic. Geochimica et Cosmochimica Acta **41** (1977) [8] 1105–1118

[4] Hart, S.R.; Davis, K.E.: Nickel partitioning between olivine and silicate melt. Earth and Planetary Sci. Letters **40** (1978) [2] 203–219

[5] Irving, A.J.: A review of experimental studies of crystal/liquid trace element partitioning. Geochimica et Cosmochimica Acta **42** (1978) [6] 743–770

[6] Berjonneau, J.; et al.: Determination of the liquidus temperatures of ashes from the biomass gasification for fuel production by thermodynamical and experimental approaches. Energy and Fuels **23** (2009) [12] 6231–6241

[7] Weidong, L.; et al.: Study on the ash fusion temperatures of coal and sewage sludge mixtures. Fuel **89** (2010) [7] 1566–1572

[8] Poirier, J.; et al.: An overview of refractory corrosion: observation, mechanisms and thermodynamic modelling. Refractories Applications Transactions **3** (2007) [2] 2–12

[9] Poirier, J.: Recent tendencies in refractories in relation with services conditions in the steel industry. Proc. of the 39th Int. Colloquium on Refractories, Aachen (1996) 6–16

[10] Meyer-Rau, S.; Telle, R.J.: Testing strategies for corrosive interactions of ceramics with semi-solid and molten metal alloys. J. of Europ. Ceram. Soc. **25** (2005) [7] 1049–1054

[11] Peregrina, C.; Large, M.: Caractérisation de la partie minérale des boues de STEP, Suez environnement (2009)

[12] Bourgel, C.; et al.: Behaviour of phosphorous and other inorganics during the gasification of sewage sludge. Energy and Fuels **25** (2011) [12] 5707–5717