CALCITE FLUIDIZED BED REACTOR HEATED BY ARGON-HYDROGEN PLASMA JETS FOR THE DESTRUCTION OF CARBOFLUORINE WASTES .

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ABSTRACT.

Thermodynamics calculation of the pyrolisis of a test molecule CF_4 have shown that the lowest levels of toxic species were obtained by using Ar-H_2 plasmas. In this case no toxic molecules such as phosgens could be formed as long as no air leakage in the reactor, occured, but this pyrolysis resulted in high quantities of agressive species such as HF (main specie) CHF, C_2HF.... To trap the free fluorine atoms responsible of these species formation, calcia was used resulting in the formation of CaF_2. The viability of these calculations was tested by building a fluidized bed heated by a D.C. plasma jet in which CF_4 was injected. The first tests have shown that the best configuration was obtained with a classical fluidized bed where alumina or calcite particles (d=300µm) were fluidized by argon gas in which a D.C. plasma torch, disposed tangentialy at the bottom of the bed, stirred and heated the particles. By using D.C. vortex plasma torches working with nitrogen very uniform temperature distributions were obtained which could be varied between 700 and 1600 K. The torch was then modified to work with Ar-H_2 and the test with CF_4 injection are in progress.

INTRODUCTION.

As demonstrated by different autors [1 à 6], mainly through thermodynamic calculations, the heating of different toxic wastes containing C and F or Cl result in the formation of rather toxic species (phosgens, cyanides, ...) and or agressive ones (HF, F....). An elegant solution was proposed by Amouroux [5] consisting in trapping the fluorine atoms as calcium fluoride in $CaCO_3$ or CaO fluidized beds heated by a plasma jet where the toxic wastes were injected and decomposed. This paper will be devoted to the preliminary results obtained in the development of this technique :

- design and working conditions of the fluidized bed,
- thermodynamic calculations of the composition of a test molecule CF_4 injected in plasma jets with the possible reaction of the products with CaO or $CaCO_3$.

2. FLUIDIZED BED REACTOR.

After a literature survey of plasma fluidized bed reactors [5 - 13], different designs were tested in the laboratory and the last one, depicted in fig. 1, seemed to be the best to improve the stirring between the particles and the plasma jet.

The reactor was composed of three functional parts:

- the fluidized bed with a fluidization grid and the reactor chamber with the tangential plasma torch inlet. In this design the plasma torch was placed tangentially to the reactor wall in order to give a rotational movement to the particles,
- the plasma torch,
- a cyclone at the exit of the reactor collecting most of the elutriated powders.

This cyclone was also used to feed the fluidized bed tank with powder once the plasma torch has been started.

The operation scheme was the following:

- first the fluidizing gas was introduced in the empty reactor chamber with the flow rate corresponding to the minimum fluidization (a few tens of slm),
- the plasma torch was then started to avoids any plugging of the torch by the fluidized bed powders,
- at last the fluidized bed powders were progressively introduced and fluidized by the gas coming through the grid. Their centrifugation started when their level in the reaction chamber reached that of the torch nozzle.

The first experiments were performed with either a D.C. spraying plasma torch working with Ar-H_2 or a vortex type one working with N_2 . The influence of the torch design, nozzle diameter, power level and gas flow rate was systematically studied. The results have shown that the heating of the bed is the most regular when the plasma jet momentum is high and its temperature as low as possible i.e. when using a vortex type plasma torch especially

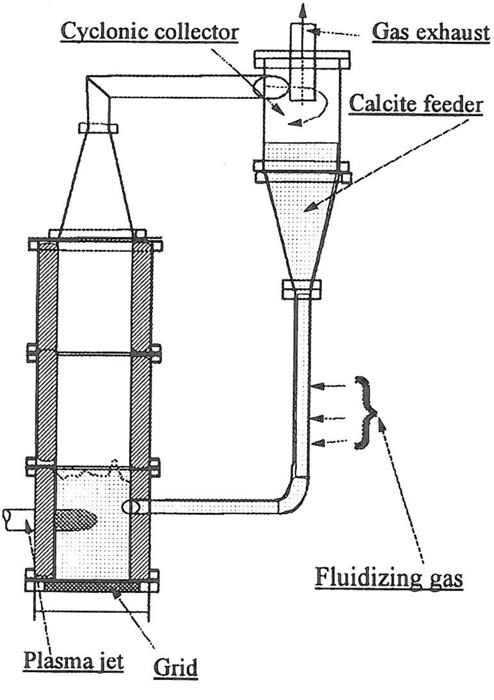

Figure 1. Schematic of the vortex recirculating reactor

designed for this application [13,15] and which working parameters with Ar-H_2 are presented in another paper at ISCP 12. With this torch working with N_2 a good centrifugation with almost no melting of the fluidized bed particles was achieved resulting between 700 and 1400 K in a uniform heating of the bed and no agglomeration of particles.

With the vortex torch with a nozzle internal diameter of 8 mm the measurements performed by Roumilhac[13] (molecular spectrocopy of N_2) have shown that the maximum temperatures for typical working conditions (I=200 A, V=120 V, y=65%, $m°_{N2}$ = 40 slm) were 8000K, against 14000K for praying torches, with a rather radial flat profile. For these working parameters the maximum velocity of 400 m/s [16] and its radial profile was also flat. This was due to the efficient vortex and the long anode nozzle (110mm). In these conditions test were made with $CaCO_3$ powders which size distribution was - 100 + 500 µm. They were fluidized with 60 slm N_2 and the torches power level was limited to 24 kW.

The fluidization and the stirring of the bed were excellent with a uniform heating at 1300 K and a rather low elutriation. However as it could be expected from the calculations of Arnould [10] and Palandri [17] $CaCO_3$ was transformed in CaO after a working time of about 5 to 6 mn.

3. FLUORINE ATOMS STORY.

The main problem of the destruction of waste fluorocarbon is: what happens to fluorine atoms? And how can they trapped by species such as CO to form phosgens for exemple?

Pernin et al. [5] have studied the system CF_4-O_2-H_2 were the main toxics are CFO_2, CFO, FO, and shown that as soon as oxygen was present the phosgens were unavoidable at temperatures between 300 and 3000 K. Thus in the following we have performed a systematic study of the composition of different plasma gases with CF_4 with or witout solid particles of $CaCO_3$ and CaO in this temperature range.

3.1-CALCULATION OF COMPOSITION AT THERMODYNAMIC EQUILIBRIUM.

Depending on the temperature, pressure, and initial mole fractions, a set of equations is solved simultaneously in order to determine the densities of the different species. The method used consisted in minimizing the Gibbs free energy G with mass conservation and electrical neutrality equations. The minimization was achieved by using Lagrange's multipliers, and the solution of the corresponding set of equations was based on the White and Dantzig [18,19] steepest descent method. The developed computer code can be run with solid or liquid species. Knowledge of the partition functions of the different species was a prerequisite to the calculation. Therefore, these partition functions were determined (see for exemple [19]) for H_2, O_2, F_2, H, F, CO, N_2, N, CN and HF by using the electronic, vibrational and rotational energy levels and spectroscopic data from literature. For the other species the tables of JANAF [19] were used. However it is worth to underline that rather big discrepancies exist between various tables especially for minor species. The considered species in gas phase are given in table 1.1 and the condensed ones in table 1.2:

H	H2						
C (s)	C	C2	C3	C4	C5		
N	N2						
O	O2	O3					
F	F2						
HF	F2H2	F3H3	F4H4	F5H5	F6H6	F7H7	
FO	FO2	F2O					
CF	CF2	C2F2	C2F4	CF3	CF4		
OH	HO2	H2O	H2O2				
NH	NH2	NH3	N2H4				
CH	CH2	CH3	CH4	C2F6	C2H	C2H2	
CN	CN2	C2N	C2N2	CNC2H4		C2H6	C3H8
CO	CO2	C2O	C3O2				
NO	NO2	NO3	N2O	N2O3	N2O4	N2O5	
COF2	COF						
FHO							
CHF	C2HF	CH3F	CH2F2				
HCOF	CF3OH						
HCO	CH2O	CH3OH		CH3OH(l)			
HCN							
NOF	NO2F						
HNO3							

Table 1-1: Different species considered in thermodynamic calculations.
(except when mentionned, the species are gaseous species).

$CaCO_3$ (s) aragonite	CaF_2 (s)	Ca (s)	CaC_2 (g)
$CaCO_3$ (s) calcite	CaF_2 (l)	Ca (l)	
CaO (s)	CaF_2 (g)	Ca (g)	
CaO (l)			

Table 1.2 List of the Species with Calcium: (s) Solid, (l) Liquid, (g) Gas

In order to determine the mole numbers of toxic species which are formed, essentially below 3000K, compositions were determined up to 3000 K and all calculations were performed at 10^5 Pa. In the figures presented below in most cases to make them more readable, only the mole number of species with fluorine have been represented.

.3.2.Results.

a) CF_4-Air.

To confirm the results of the literature showing that the presence of oxygen promotesthe formation of phosgens, fig2a represents the composition for a mixture $CF_4+O_2+4N_2$ (the number represents the initial mole number). It can be seen that CF_4 is completely destroyed by combustion with air. The energy of combustion makes easier the formation of NO which exhbits a maximum at 1800K. Unfortunately when looking at species with fluorine many toxic products are formed among which : COF,

COF_2, NOF represent pratically the main species with F atoms over 1500K. At temperatures higher than 2100K, it can be noticed the significant formation of products such as FO_2, FO, NO_2F. It has to be undeclined however that in most pratical cases in plasma only rather small mole fraction of CF_4 will be introduced.

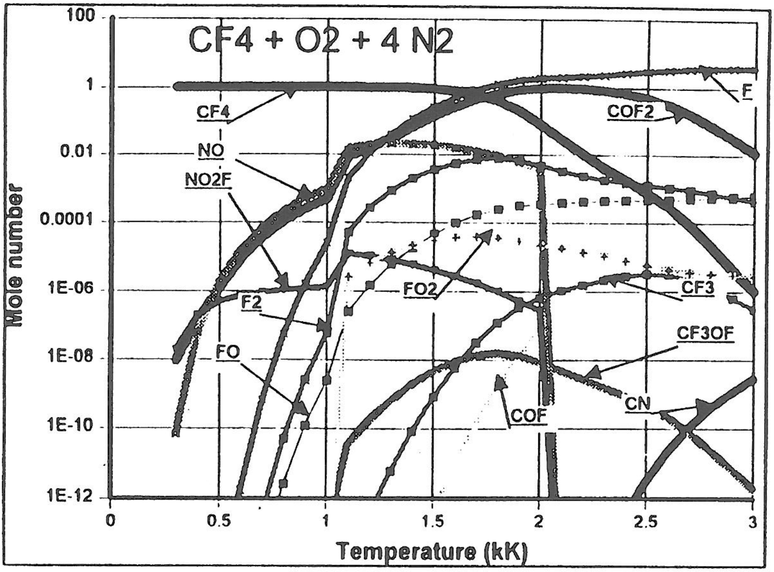

Figure 2. Evolution with temperature at 10^5 Pa of the numbers of the species containing fluorine atoms
a/- CF_4+ air

b) CF_4+Ar or N_2.

When using pure argon with which no toxic product can be formed, the calculations show it is completely inefficient and that below 3000K the main species is undecomposed CF_4.

It is the same with nitrogen as plasma gas which moreover induces the production of cyanides at temperatures higher than 2000K.

c) CF_4+air +10 $CaCO_3$

Figure 2b represents the corresponding composition below 1600K, most of the fluorines atoms are trapped as CaF_2 which becomes liquid at about 1700K

The level of the toxic phosgens is low (below 10^{-6} moles), however the cyanides level reaches 10^{-8} moles.

d) CF_4+10 $CaCO_3$ +3 H_2

Figure2c shows that, as previouly most of the atoms are trapped as CaF_2 but the formation of HF is not quite negligble and for temperature higher than 1700K, probably due to the decomposition of $CaCO_3$ and the reaction of CO with HF, the formation of phosgens is not at all negligible (up to 10^{-2} moles).

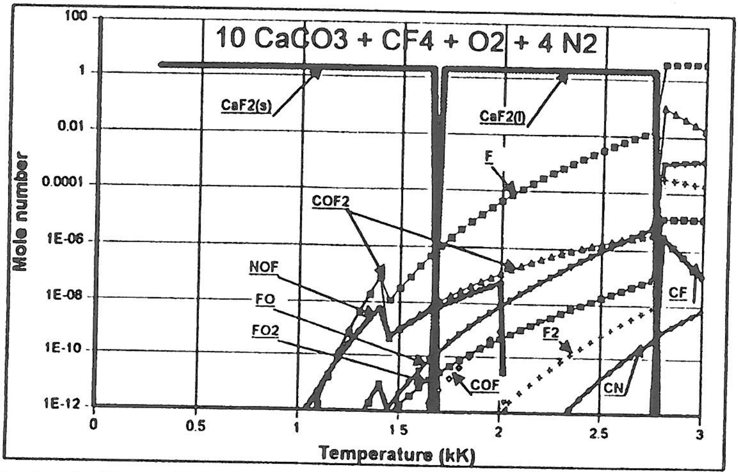

Figure 2. Evolution with temperature at 10^5 Pa of the numbers of the species containing fluorine atoms
b/- CF_4 + air + 10 $CaCO_3$

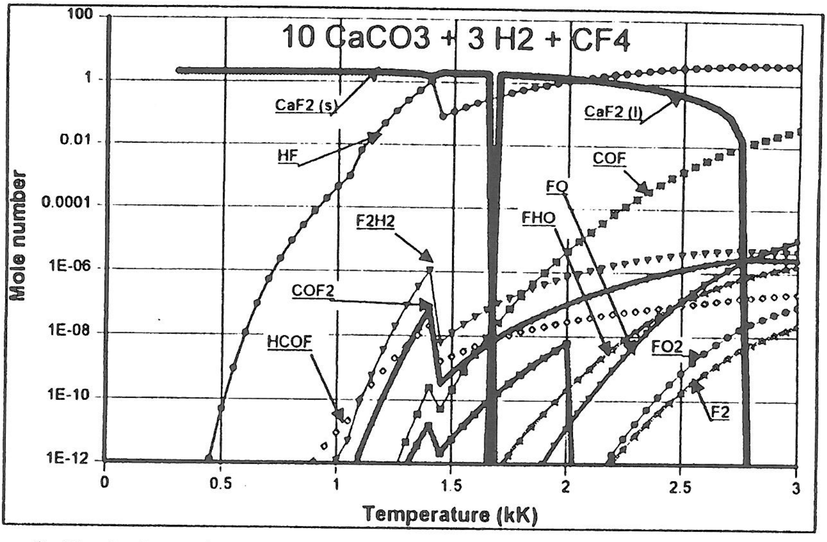

Figure 2. Evolution with temperature at 10^5 Pa of the numbers of the species containing fluorine atoms
c/- CF4 + 10 $CaCO_3$ + 3 H_2

e) CF_4+Ar+3 H_2+CaO

The results presented in figure 2d show that the phosgens level is below 10^{-8} moles even when CaF_2 has been completely decomposed. It is worth to note that if the hydrogen mole number is below that allowing to trap all the fluorine atoms from CF_4 as HF the level of phosgens increases drastically when CF_4 decomposition occurs.

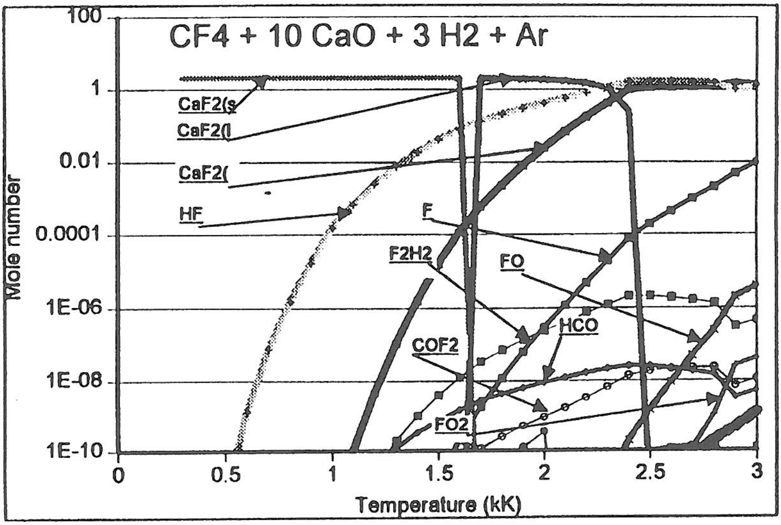

Figure 2. Evolution with temperature at 10^5 Pa of the numbers of the species containing fluorine atoms
d/- $CF4 + 10 CaO + 3 H_2 + Ar$

4. CONCLUSION

A fluidized bed reactor heated by a d.c. plasma torch was designed where fluidization and heating were two separated functions. The plasma torch was disposed tangentially, close to the bottom of the bed, participating to its stirring resulting in a rather uniform temperature (less than 5% difference between temperatures measured respectively close to the bed axis and its wall). The use of a dc vortex plasma torch with a hot buttom type cathode has allowed to obtain nitrogen plasma jets which temperature was below 8000K with velocities varying from 400 to 1000 m/s for power levels between 14 and 50 kW. The velocity and temperature radial distributions had rather flat profile ($\Delta T/T < 15\%$ and $dV/V < 10\%$). It is then expected that the CF_4 injected in such plasma jets will undergo a more uniform heat treatment. The thermodynamic calculations with $CaCO_3$ or CaO fluidized beds have shown that CaO traps very easily fluorine atoms reducing correspondingly the formation of toxic species. The lowest values of toxic species were obtained with Ar - H_2 plasmas with a CaO fluidized bed. However over 1700K CaF_2 is decomposed and if there is not enough H_2 to form the phosgens mole numbers increase.The first experiments with $CaCO_3$ fluidized beds heated by N_2 plasmas have shown that after 20 mn such beds are mostly constitued of CaO particles in good agreement with kinetic calculations [10,17]. The vortex plasma torch has been modified to work with Ar - H_2 mixtures containing more than 50 vol %H_2 experiments are now in progress. The $CaCO_3$ fluidized beds are heated during 10 mn to decompose $CaCO_3$ into CaO and with a plasma torche working with Ar-H2 (60 vol%) plasma forming gas (100 slm) in which a few slm CF_4 are injected.

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Ackowledgment: This work was supported by CNRS, ADEMI and EDF with the frame of ARC "Plasma Thermique Appliqué au Traitement des Rejets" Programme ECOTECH

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