CONCENTRATED OXYGEN - OZONE MIXTURES STABIILITY AT HIGH PRESSURE

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1 - INTRODUCTION.

Since many years, ozone is used in water treatment at relatively low concentration and low pressure. There is now a great interest to use ozone at high concentration and high pressure. The main industrial application is the bleaching of pulp, in which ozone is replacing chlorinated bleaching agents. For bleaching of medium consistency pulp, ozone is used at pressures up to 10 or 15 bar g and concentrations of 10 wt-% or more, according to the possibilities of the ozone generators and the bleaching equipment.

This article examines the behaviour of ozone - oxygen mixtures at concentrations up to 16 wt-% and 20 bar g under static conditions as part of a study aimed at defining conditions ensuring a totally safe handling of ozone.

2 - LITERATURE REVEEW.

Ozone is a metastable molecule, whose conversion to oxygen liberates 143 kJ/mole, i.e. 2.98 kJ per gram of ozone. The rate of decomposition increases with temperature. The question arises whether, once initiated, the decomposition of ozone in high concentration ozone oxygen mixtures can propagate sufficiently rapidly to cause an explosive, i.e. nearly instantaneous, decomposition of all the ozone present in the mixture. If the reaction front propagates at speeds of the order of I cm/s to 100 m/s, one uses the term "deflagration" ; at propagation speeds in the order of 1000 to 3000 m/s, one speaks of "detonation". In the case of deflagrations, pressure gradients in the reaction vessel remain small, and the ratio of maximum to initial pressure is

limited to about 10 or less. Detonations, in contrast, produce strong pressure gradients and pressure ratios about 2.5 times larger than deflagrations.

Lewis and Von Elbe [1,2,3,4] reported that ozone - oxygen mixtures containing 40.06 mole-% (at an initial pressure of 367 mm Hg (0.49 bar a)) and 41.9 mole-% of ozone, ignited with a platinum wire, lead to detonations. The maximum pressures reached were respectively 3029 mm Hg (4.04 bar a) and 3060 mm Hg (4.08 bar a). The time between ignition and the establishment of maximum pressure was around 0. 01 seconds.

Harper and Gordon [5] studied ozone - oxygen mixtures at initial pressures ranging from 497 mm Hg (0.66 bar a) for low concentrations, to 110 mm Hg (0.15 bar a) for mixtures containing 77 mole-% (i.e. 83.4 wt-%) of ozone. They describe three ranges of concentrations

- Below 9.2 mole-% (i.e. 13.2 wt-%), no detonation was observed.

-Between 9.2 mole % and 60 mole-% (i.e. 69.2 wt-%), a detonation can occur if initiated by a (hydrogen - oxygen) predetonation. Typical detonation speeds from 900 to 1700 meters per second were measured. The observed pressure ratio between the maximal and initial pressure ranged from 4.5 to 20. These experimental ratios were several percent lower than the theoretical ones.

- Above 60 mole-%, a spark. was sufficient to trigger detonation. Detonation speeds increased from 1700 to 1836 meters per second for 77 mole-% (i.e. 83.4 wt-%) ozone mixtures. Pressure ratios were measured between 20 and 23.5, also lower than the theoretical ones.

It is of interest to note that in spite of geometries and experimental conditions favourable to detonation, such behaviour could not be provoked at concentrations below 13 wt-%.   -

Wailer and McTurk [6] reported that ozonised oxygen containing 10 wt-% of ozone can be compressed safely to 70 bar.

3 - APPARATUS & EXPERRMENTS.

Figure I is a schematic view of the different parts of the experimental set-up used in the present work.

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The cylindrical test vessel installed between valves V5 and V7 is constructed in 316-L stainless steel and has an inner diameter of 55 mm and a length of 121 mm- All lines are in 316-L stainless steel or in P.T.F.E.

Oxygen

Ozone
Generator

Bypaso

V4

vi

Water

Exploding
Wire

Bypass

V2

A typical test is achieved by the following **main steps :**

Ozone
Destruction

exha@
Gas

Figure I

-The system (serpentine, vessel, analysis lines) is first purged with the ozone oxygen @ures at the desired concentration. When the concentration at the outlet of the system is equal to the one at the outlet of the ozone generator, the valves V7 and VI are closed. V4 is opened.

 - The gas mixture is then compressed by feeding water into the serpentine with a manual pump (V2 is opened). This type of compression allows a quasi isotherinal compression to take place. The compression is stopped and the pneumatic valve V5 closed when the desired pressure for the test is reached.

- Two different types of test can now take place :

    The gas mixture can be maintained at the test pressure for a certain time .
    (typically I 0 minutes to I hour) without any attempt to trigger decomposition.

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The gas nurture can also be "fired". In this kind of **test,** we try to initiate the ozone decomposition by introducing a energy of 100 Joules into the vessel. This energy is delivered by a tungsten wire which explodes when its temperature reaches 3410'C. During the test, pressure and temperature are recorded by means of a recorder and an oscilloscope. The test is completed when the temperature has decreased to near its initial room-temperature level. This typically takes 5 rninutes.

- The system is then depressurized by lowering the water in the serpentine. This procedure avoids possible ozone losses through pressure reduction valves. When the pressure in the vessel reaches 2.5 bar g., the remaining gas is sent to the analyser.

- After each **test,** the whole system is cleaned vath acetone and dded using hot nitrogen.

The main equipment characteristics are su=arised in the following table.

Ozone Generator	OZONIA-LN 103 Advanced Technology No@nal Ozone concentration: 1 0 wt-% Maximum Ozone Concentration: 20 wt-%
Pressure Gages (Ropill)	Haehni : Response time: 3 0 ms Schaevitz : Response time 25 ms
Platinum Temperature Gages **(lftiol)**	Engelhard-Pyrocontrol Type PT I 00. Diameter 1.2 mm
Ozone analysers	BMT 961 Maximal Ozone Concentration: 400 g/Nm3 (i.e. 25.6 wt-%) Response Time: 1 00 ms Continuous Analyser (UV)
Oscilloscope	Nicolet type 3 1 0

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4 - RESULTS & DISCUSSION,

4.1 - Tests without ignition.

Ozone - oxygen mixtures containing up to 16 wt-% of ozone were stored during a maximum of one hour at a maximum pressure of 20 bar g. The relative loss in concentration after this one hour storage never exceeded 11 % of the initial ozone concentration.

-Pecomposition after 10 minutes storage at 20 bar g was negligible.

4.2 - Tests with ignition.

a) General observations.

During our experiments, we never observed any detonation in agreement with the findings of Harper and Gordon [5]. The time between the ignition and the establishment of the maximum pressure was measured in the range 0.5 to 1.5 seconds. This time is relatively independent of the pressure. It seems to show that we are in a slow deflagration mode (since the distance between the exploding wire and the pressure gage is around 5 cm, the front velocity is found to be around 3 to 10 cm/S).

b) Ozone destruction.

Figure 2 shows the fraction of the initial ozone decomposed after the ignition.

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100

90

80

50

1

30

20

10

@ @:@ @:   @ :: @: I @::: @ @   ;   :: @:

-@@ W[TJ @ IGNI   N ,

...

2 4   6 8 10 12 14 16 18

03 w concentration (wtm%)

Figure 2

There are two different behaviours **of the ozone - oxygen @xture depending on the pressure.**

At near atmospheric pressure, the destruction after ignition stayed low : relative ozone loss remained below 2% on the 5 minutes-scale of these experiments.

For mixtures compressed at 5 to 20 bar g, we can define three zones depending on initial concentration .

- the first zone below about 7 wt-% of ozone, in which the destruction never exceeds 25 % of the initial ozone concentration.

- **a** second zone above about 13 **wt-%,** in which **the ozone loss is always** in **the range 75 to** 95 %.

- a third transition zone, between about 7 and 13 wt-%, in which the behaviour of the gas nurture is very scattered.

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These observations are consistent with a picture where the ozone in the neighbourhood of the exploding wire undergoes rapid thermal decomposition. At the higher concentrations, the energy released by this exothermic reaction propagates throughout the gas volume until all the ozone is destroyed. At lower concentrations, this chain reaction is quenched by carrier oxygen and the energy is dissipated to the walls of the vessel.
At intermediate concentrations, the outcome will depend on the manner in which the exploding wire disperses the initial 100 Joules in the reaction volume.

c) Pressure increase

Figure 3 shows a typical oscilloscope trace of the observed pressure variation (15.45 wt-% ozone mixture at an initial pressure of 20.91 bar a)

70

50 -

@   40-

CO

ma   -
t   A

30 -
    0
    .a   -
    Cb

10

Ignition

PM&X

Pfinal @

0   [
  0.0   i   I-   I   I   4.0
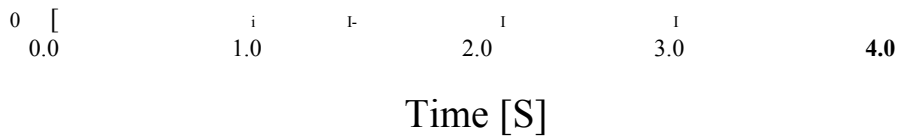 0.0   1.0   2.0   3.0

Time [S]

Figure 3

The asymptotic pressure - Pfinal - provides for a consistency check of the concentration measurements, since, once the system has retumed to the initial temperature, the pressure increase reflects on the amount of ozone decomposed (2 03 --> 3 02).

The observed final pressures agreed with the values calculated from the measured final temperature and composition changes within < 1%.

The maximum pressure - Pmax - observed shortly after the exploding wire is flashed, is plotted in figure 4 as a function of initial pressure and ozone concentration. Its values can also be calculated from the measured concentration loss, knowing the exothermicity of the decomposition reaction, by assuming that the ozone that does decompose does so sufficiently rapidly for heat losses to the vessel to be negligible.

50

10

8

C)3 - concentration (wt-%)   **4**

2   0

Pmax (bar a)

so

20

10

15
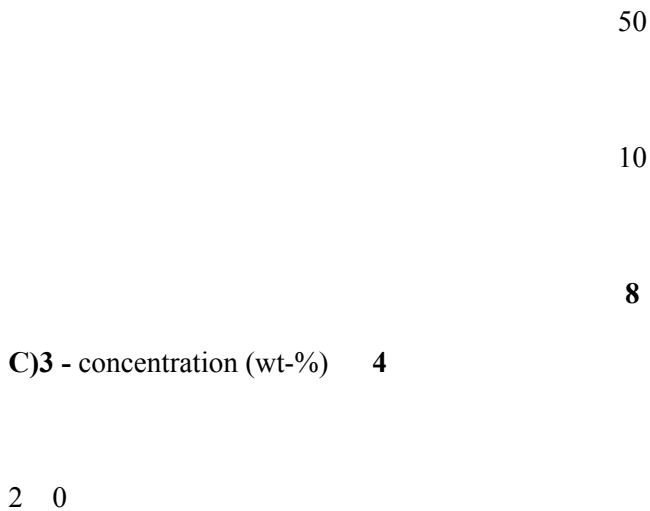
10 Pini **(bar a)**

Figure 4

As shown in figure 5, the observed pressure ratios (Pmax/Pini) are typically < 20% lower than those calculated, presumably because of heat losses to the vessel walls.
Thus, the calculated numbers give a conservative estimate of the maximum pressure that could be reached under the relevant experimental conditions.

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3.5

o@.5

1.5

3.5-

*2 2.5
rL

*R

9

@ 1.5

obsd.
calc.

Pini=5bar g

6 7 8 9 10 11 12 13 14 15 16 17
03-concentration (wt-%)

obsd.
calc.

- - - - - - - - - - - - - *Pini= 15bar g*

o:

gIt if I Ipie I I   I go tilt I I   I I it I I it I1 flit

6   7   8   9   10   1 1   12   1 3   14
03-concentration (Wt-%)

3.5

0

A 3
CL
o@-5

1.5

3.5

7E 2.5
a:
oj

1.

L.

cg 2

k *1.5*

o@.

calc.

Pini= 1 **Obar g**

2 0 0**t** OAR I   f

6   7 8   9 10 11 12 13 14   15   16 17
Concentration **(wt-%)**

obsd.
calc.

I

....

- - - - - - - - - - - - - *Pini*
-20bar g

6   7 8   9 10 11 12 **13 14 15 16**
03-concentration (wt-%)

Figure 5

The pressure ratio (P maximum / P initial) is relatively independent of the initial
pressure but increasing with the initial ozone concentration.

5 - CONCLUSIONS,

At near atmospheric pressure, we have not found any contra-indication for the **use** of ozone **at**

concentrations up to 16 wt %, the highest value investigated 'n the present work.
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For ozone-oxygen mixtures under pressure (up to 20 bar g), significant ozone decomposition was
only observed at concentrations above about 7 wt-%, and this only when triggering this
decomposition by using the exploding wire.

We never observed indications of a detonation.

The maximum pressure increase in the system was always lower than that calculated from the
observed concentration loss and the energy released in the system by the exploding wire plus
the decomposition reaction.
For a 10 wt-% ozone mixture, at initial pressure and temperature of 10 bar g and 25'C
respectively, the maximum pressure increase will be of 20 bar, if total decomposition occurs
throughout the gas volume.

In industrial ozone distribution networks, this represents a conservative worst-case scenario.
Further investigations are under way to simulate the repercussion of local ozone decomposition
on flowing streams of ozone-oxygen mbctures.

Keywords

Oxygen - Ozone - Safety - Decomposition

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