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Research article

Formation of Ni and Mg vanadates during the flameless oxy-combustion of heavy fuels

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ABSTRACT

Flameless oxy-combustion is a very efficient technology for treating low-ranking fuels with energy recovery, when operating in the high temperature range of 1200–1600 °C. However, the thermal valorization of these low-ranking fuels, containing a significant amount of vanadium, causes some problems due to the volatility and corrosiveness of V_2O_5 with ceramic and metal alloys at high temperatures. The formation of mixed V/Mg or V/Ni compounds, which are stable at high temperatures (1300 °C), was investigated in a tubular lab-scale furnace with a residence time of 2 s, starting from sprayed aqueous $VOSO_4$, $MgSO_4$, and $NiSO_4$ solutions. It was seen that $MgSO_4$ and/or $NiSO_4$ led first to the formation of MgO and NiO, which then reacted with V_2O_5 to produce fully inert $Mg_2V_2O_7$, $Mg_3V_2O_8$, and $Ni_3V_2O_8$. The experimental data were combined with thermodynamic equilibrium calculations, to predict the stability of the vanadates obtained.

1. Introduction

Among the environmentfriendly combustion technologies developed over the past few years, high-temperature flameless oxy-combustion has attracted a great deal of attention due to its positive performance characteristics such as high-energy recovery efficiency, combustion stability, temperature uniformity, flexibility, and low formation of pollutant species [1–6]. Under pressurized conditions – with a combustor coupled with a steam recovery boiler in a pressurized fume loop – this technology makes it possible to obtain the oxy-combustion of a broad spectrum of fuels in the 1200–1600 °C range, with a fuel residence time from 2 to 10 s. At these temperatures, the incombustible particles of the fuel melt, coalesce, and settle from fumes, draining to the bottom of the reactor as molten slag, which may turn into solid, fully inert, vitrified slag by cooling outside the reactor [7–11]. Thus, at the working temperature, this technology drastically abates fly ashes in fumes.

Flameless oxy-combustion makes it possible to treat difficult fuels, for example coals characterized by different mineralogical compositions [12–15] or waste-heavy/carbonaceous fractions deriving from the processing of crude oils (i.e. asphaltenes) or fossil fuels (i.e. shale oils or tar sands) containing significant amounts of sulfur and heavy elements. In particular, many crude oils, especially those from South America, contain high amounts of V or Ni, together with other elements (Fe, Zn, Cu, Pb, Mo, Cr, Mn, Co, and As). These elements are present mainly in a specific group of cage-like compounds, called porphyrins.

The element content in oils is dominated by Ni and V, from less than 15 ppm in some Saudi Arabian light crudes [16] up to 1200 ppm of V and 150 ppm of Ni in the Boscan crude oil from Venezuela [17]. During crude oil fractioning, element-containing porphyrins preferentially migrate to asphaltenes; the high content of V and Ni makes it impossible to burn these latter fractions because these elements promote the formation of ultra-fine particles in the operating conditions of traditional combustion processes [18].

Flameless oxy-combustion technology appears to be a valid solution for energy valorization in the heavy fractions deriving from the processing of crude oils or fossil fuels, but it is necessary to remedy the specific drawback of V: its aggressiveness at high temperatures. In fact, at high temperatures, V induces a hot corrosion of the ceramic materials constituting the insulating layer of the combustion chamber, especially in the presence of Na. Furthermore, the highly volatile V_2O_5 going with the fumes into the boiler may corrode the element components.

Previous papers have been focused on additives introduced into fluidized bed combustors and gasifiers for the purpose of decreasing or avoiding surface deposition, agglomeration, sintering, and corrosion by heavy elements [19–21]. In gas turbines, the usual approach for limiting V-induced hot corrosion is to trap V, either in the flame or

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Table 1
Composition of the aqueous solutions fed in the experimental tests.

Test number	Elements	$VOSO_4$ mol/L	$MgSO_4$ mol/L	$NiSO_4$ mol/L	Mg/V mol/mol	Ni/V mol/mol
1	V	0.100	0.000	0.000	0.000	0.000
2	V, Mg	0.100	0.125	0.000	1.250	0.000
3	V, Ni	0.100	0.000	0.150	0.000	1.500
4	V, Mg, Ni	0.200	0.125	0.150	0.625	0.750

downstream from the flame, in refractory compounds with high melting points, by adding additives [22,23].

Since the 1970s, MgO has been commonly used as an additive in fuels, especially in gas turbines, for V mass-trapping. In the flame, Mg-based compounds give rise to MgO, which reacts with V_2O_5 to produce the refractory $Mg_3V_2O_8$ (melting point = 1074 °C) [24–27]. Thus the amount of corrosive ashes on the element parts is drastically reduced, although the amount of total ash material in the thermal equipment greatly increases. Indeed, in practice, a Mg/V ratio greater than 3 wt.%, higher than the stoichiometric ratio of 0.7 in $Mg_3V_2O_8$, is necessary to obtain an acceptable inhibition efficiency. The high Mg/V ratio required is due to the partial sulfation of MgO to $MgSO_4$ caused by the contact with the combustion gas containing SO_2/SO_3 species [26–28] at working temperature in traditional systems, approximately 800–1000 °C. Thus, considering the high S amount present in asphaltenes, traditional combustion technologies cannot be applied due to the significant sulfation of additives. Conversely, in the operating temperature range of flameless oxy-combustion technology, 1200–1600 °C, the sulfation of magnesium oxide is very limited [29] while nickel sulfate is fully decomposed [30].

A previous work focused on both batch thermochemical experiments with mixtures of V_2O_5, Na_2SO_2, NiO, or MgO, and corrosion tests on a superalloy in contact with these mixtures in the 550–850 °C range [31]. The addition of NiO produced the refractory compound $Ni_3V_2O_8$ (melting point = 1310 °C), which reduced the corrosiveness of ashes by trapping vanadium. On the other hand, the addition of MgO gave rise to $NaMg_4(VO_4)_3$ or $Mg_3V_2O_8$, which stabilized the orthovanadate anions (VO_4^-), while reducing the corrosive effect of most acid VO_3^- and V_2O_5 species.

Table 2
Summary of operating conditions.

Temperature (°C)	1300
Residence time (s)	2
Time-on-stream of each test (h)	24
Flow rate of the liquid phase (ml/h)	20
Volume of aqueous solution fed (ml)	480
Carrier gas	CO_2/O_2 (90:10 v/v)
Operating pressure	1 bar
Filter capability	Particles with diameter > 0.1 μm
Aqueous solutions in the traps of the gas absorption set	HNO_3 0.1 M

This paper analyzes the effect of nickel and/or magnesium addition on the chemistry of vanadium at high temperatures (1300 °C) and with a residence time of 2 s in a lab-scale tubular furnace, thus simulating the operating conditions (temperature and residence time) of a flameless oxy-combustion plant. In the tests, the sulfates of Ni or Mg were fed to take into account the effect of the S-content while hypothesizing their almost complete decomposition in the test conditions. For verification purposes, a preliminary thermodynamic equilibrium modeling was carried out to predict the chemical speciation of the system, including the decomposition equilibrium of sulfates and the SO_2/SO_3 equilibrium in the range 600–1600 °C. Experimental tests were then performed to observe the trend of the hypothesized reactions at high temperatures (1300 °C).

2. Material and methods

2.1. Materials

Tests were carried out by feeding four aqueous solutions (Table 1) containing commercial-grade (Sigma-Aldrich) $VOSO_4$, $NiSO_4$, and $MgSO_4$. Theoretically speaking, the concentration ratio of solution no. 2 was such that 50 wt.% of V could form $Mg_3V_2O_8$ and the remaining

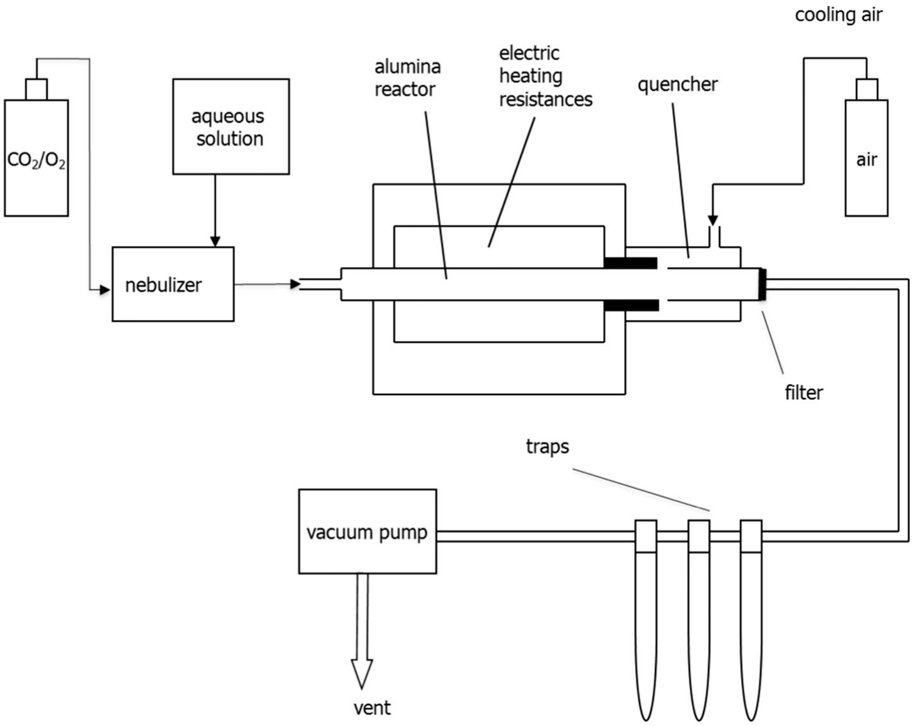

Fig. 1. Schematic description of the experiment equipment.

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