TESTING OF CARBON MONOXIDE OXIDATION ON THE COPPER OXIDE UNDER VARIOUS CONDITIONS

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The helium coolant of gas-cooled nuclear reactors is being continually contaminated by gaseous and solid impurities. In purification circuits of the reactors carbon monoxide (CO) and hydrogen are converted in an oxidizing bed on CuO pellets into carbon dioxide and water and these impurities are then captured in a molecular sieve bed. Oxidation capacity of CuO is crucial when designing the oxidizing bed of a purification circuit. Experiments with various volume fraction of CO in helium gas mixtures were carried out in order to determine oxidation capacities of CuO. Experiments were performed on an apparatus with a heated cell and the gases were analyzed on a FTIR. Oxidation capacities of CuO under various conditions were calculated.

1. Introduction

Increasing global population leads to higher energy consumption. The need for finding new energy resources is growing, because conventional fossil fuels are limited in supply and will be depleted. Generation of electricity in nuclear power plants by nuclear fission doesn't create any direct carbon dioxide emissions. Amount of nuclear fuel used for generation of certain amount of energy, compared to the fossil fuels, is smaller due its high energy density. Therefore nuclear energy can be considered to be less harmful to the environment than energy obtained by burning fossil fuels.

Nowadays the generation III reactors are operational and the upcoming generation IV reactors are currently under development and will be operational in the next decades. In the early 2000s six concepts of nuclear reactors were chosen by an international expert panel. The fourth-generation reactors should meet eight defined technology goals in sustainability, economics, safety and reliability, proliferation resistance and physical protection [1].

Two of six designs are gas-cooled with helium as the coolant due to its radiochemical inertness and advantageous thermal properties. "The Gas-cooled fast reactor (GFR) has a fast neutron spectrum and will be able to operate as a breeder as well as a burner of minor actinides. The very-high-temperature reactor (VHTR) has a thermal neutron with a graphite moderator and has the advantage of providing heat at temperature compatible with hydrogen production processes and other industrial processes" [1,2].

Helium in the gas-cooled nuclear reactors can be contaminated with impurities from various sources and the impurities need to be continuously removed, thus there is a purification circuit in every gas-cooled nuclear reactor and a fraction of flowing helium is being constantly cleaned there.

• Impurities

Helium of gas-cooled nuclear reactors contains undesirable impurities. Gaseous impurities are mainly N_2, H_2, H_2O, CO, CO_2, CH_4 and O_2, but oxygen immediately reacts with other agents. Dust particles and fission products (Kr, Xe, I, Cs) are present. Most of these impurities cause early corrosion of the equipment and graphite oxidation. Dust particles can cause mechanical erosion of the equipment.

The volume fractions of impurities are relatively low ($1\cdot10^{-7}$ - $3\cdot10^{-5}$), but they can interact with each other or with materials in the primary circuit and their volume fractions may change.

Sources of gaseous impurities are various. Helium is mostly contaminated by impurities during production and transportation of the helium to the primary circuit. When the temperature rises in the primary circuit the impurities are desorbed from the structural materials of the primary circuit and from the fuel. The impurities contaminate the helium by leakage from the ambient air and during maintenance and refueling. Fission products can escape from the fuel cladding to the primary circuit. Hydrocarbons can contaminate the primary circuit from bearings of pumps [3-7].

• Purification circuits

Purification circuits of the previous gas-cooled nuclear reactors were similar to each other, although every circuit have its deviations. At the entrance of the purification circuits are mechanical filters for removal of dust

Figure 1 HTR-10 helium purification system [3]

particles bigger than 5 μm from the gas. Helium then flows to the oxidizer bed where hydrogen and carbon monoxide are oxidized to water and carbon dioxide at temperatures around 250°C. These two impurities are captured on molecular sieve beds at room temperature. Remaining impurities (N_2, CH_4, O_2, Kr, Xe) are adsorbed in low temperature adsorption beds at temperatures around -160°C. Figure 1 is a demonstration of a common purification circuit [3].

When designing a new purification circuit, knowledge of expected operating conditions, levels of impurities and types and the characterization of the fillings of the oxidation and sorption beds is crucial. In the early sixties a study about helium purification system design was made in the Oak Ridge National Laboratory. They assumed, that 50% of the CuO content will be utilized for following reaction [8]:

$$CO + CuO = CO_2 + Cu \qquad (1)$$
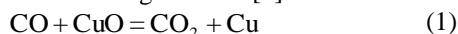
Another study conducted in the Oak Ridge National Laboratory suggested, that when hydrogen reacted with a CuO pellet, there was always a well-defined Cu-CuO interface within the pellet and that the reaction is controlled by the mass transport of the hydrogen from the bulk gas to the reaction site. Thus the reaction is very rapid and essentially irreversible [9].

There are few papers on kinetics of CO and H_2 oxidation over CuO. Plewa and Skrzypek experimentally determined the reduction rate of CuO with CO [10]. Avgouropoulos and Ioannides examined kinetics of CO and H_2 oxidation over CuO-CeO_2 and CuO catalysts [11]. Lee and Kim studied kinetics of CO and H_2 oxidation over CuO-CeO_2 catalyst in H_2 mixtures with CO_2 and H_2O [12]. Polster et al. studied the active sites and mechanism responsible for highly selective CO oxidation in H_2 rich atmospheres on a mixed Cu and Ce oxide catalyst [13]. Sadykov et al. revisited the impact of the surface state on the apparent kinetic parameters of catalytic oxidation of CO on CuO [14].

The articles on CO oxidation kinetics above indicate that CO oxidation (at low concentrations of CO) is close to the first order.

To the authors' best knowledge there is no available literature that contains information about the oxidation capacity of the CuO (percentage of CuO content utilized) for the reaction [9].

Research organizations in the Czech Republic are involved in projects concerning advanced gas cooled reactors [15 - 17]. Investigation, improvement, verification and application of helium purification techniques are within the project activities. One of the task within this program is investigation of CO (and also H_2) oxidation on suitable oxidizing agent (e.g. CuO), which is one step of the helium purification process.

2. Experimental

2.1. Oxidation experiment

Oxidation of carbon monoxide on the CuO pellets was examined. An experimental laboratory-scale apparatus was designed and constructed (on Figures 2, 3 and 4). The apparatus consisted of gas pressure reducing valves for low and high pressures, pressure gauges, pressure and flow controllers Bronkhorst F-232M, P-202C a F-033C, a heated column with CuO and a Fourier transform infrared spectrometer (FTIR) Nicolet Antaris IGS. Equipment in the apparatus was connected with stainless steel tubes. The apparatus included 4 high pressure aluminium cylinders (one with sample, that is oxidized in

the column, one with nitrogen (99.999% purity) and two with helium (99.9999% purity) that were used to flush the apparatus). The pressure and gas flow in the apparatus was controlled on a personal computer with FlowDDE and FlowWiew software in range of pressures 0 – 10 MPa and flow 0 – 33 $dm^3 \cdot min^{-1}$. The heating the column was realized by creating a tube furnace from copper sheet wrapped in heating cables and mineral wool thermal isolation (Figure 2). The temperature was controlled by Selec PID500 temperature regulators that allowed the column to warm up to temperatures around 300°C.

CuO pellets were produced by Euro Support Manufacturing Czechia. The type is ESM 468 with CuO content of 37.4 %. Composition of the pellets is shown in Tab. 1. These pellets (4.7 mm x 4.7 mm) were ground into a fraction of 1 - 2 mm for our experiments.

Tab. 1 Characteristics of ESM 468 pellets from the manufacturer

Compound	wt. %
CuO	37.4
CaO	4.3
SiO_2	35.6
MgO	15
Ni, Co	0.004
Na_2O	0.2

Series of oxidation experiments were carried out with two gas mixtures containing helium and carbon monoxide ($x_{CO} = 0.00051$ / $x_{CO} = 0.000993$).

Figure 2 Fabrication of a furnace

The mixture of helium and carbon monoxide was flowing through the heated oxidation column filled with ground CuO pellets ESM 468 and the gas flowing out of the apparatus was analyzed on the FTIR spectrometer and the molar fraction of carbon monoxide was observed. The temperature of the column was 250°C. Usable oxidation capacities were calculated from carbon monoxide breakthrough curves at various pressures. The usable capacity is the amount of CO converted to CO_2 on the CuO, until the volume fraction of the CO in the mixture flowing out of the apparatus is higher than 5 % of input molar fraction. The experiments were terminated after the molar fraction reached 5 % of the input molar fraction.

In the next experimental period the oxidation of CO on CuO will be verified in the helium purification circuit

of the High Temperature Helium Loop HTHL. More details about this semi/industrial device can be found in the citations [15,16].
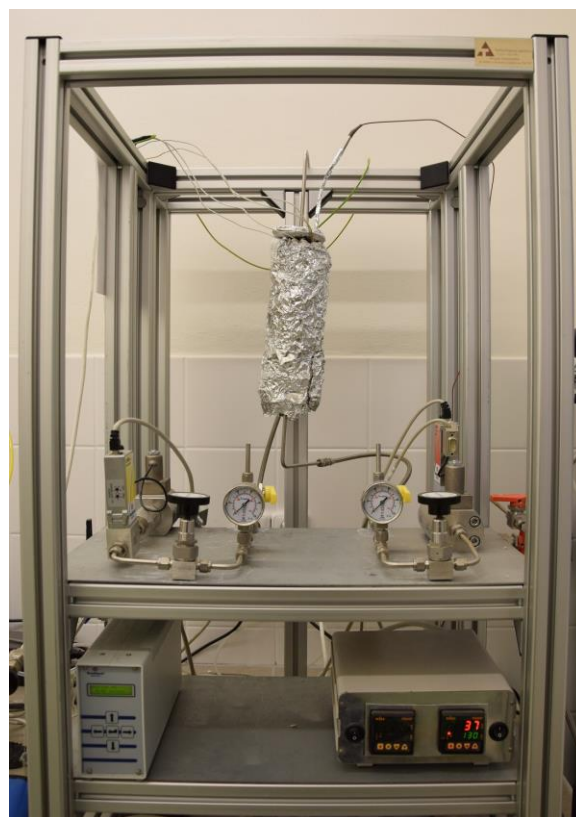

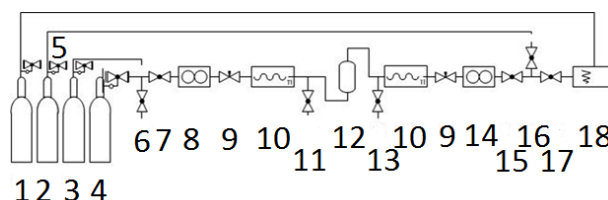
Figure 3 Apparatus with heated column

Figure 4 Diagram of the apparatus
1 - cylinder with nitrogen (99.999% purity), 2,3 - cylinder with helium (99.9999 purity), 4 - cylinder with mixture of helium and CO, 5 – gas pressure reduction valve, 6,7 - shut-off valve, 8 – pressure controller Bronkhorst F-232M, 9 – needle valve, 10 – pressure gauge, 11 – shut-off valve, 12 – heated column, 13 – shut-off valve, 14 – flow and pressure controller Bronkhorst P-202C and F-033C, 15,16,17 – shut-off valves, 18 – FTIR spectrometer.

2.2. SEM-EDX particle surface analysis

Surface changes of CuO particles cuttings used in the experiments were investigated by scanning electron microscopy (SEM) coupled with an energy dispersive (EDX) detector. The aim of the analysis was to determine possible changes in oxygen content near surface of the particles. Particles were cross-cut, the specimens were

poured into resin and the resin was polished on the cut-side of particle before SEM analysis. Subsequently a line analysis of particle composition from particle surface towards core was carried out.

3. Results and discussion

The breakthrough curves (Figures 5 and 6) were collected and usable capacities were calculated (Tab. 2) using the following equation (2) derived from the ideal gas state equation:

$$ c_u = \sum \left(\frac{\rho_{0i} - \rho_i}{10^6} \bullet \frac{\dfrac{t_{i+1} - t_i}{60} \bullet q \bullet p \bullet M}{\dfrac{R \bullet T}{m_a}} \right) \quad (2) $$

where c_u is usable capacity of 1 gram of CuO [mg·g⁻¹], ρ_0 is volume fraction of impurity in the input gas [cm³·m⁻³], ρ_i is volume fraction of impurity in the outlet gas in the time of analysis [cm³·m⁻³], M is molar weight [g·mol⁻¹], m_a is weight of the sorbent [g], t is time [s], q is flowrate [dm³·min⁻¹], p is atmospheric pressure [Pa], R is molar gas constant [8,314 J·K⁻¹·mol⁻¹] and T is temperature [K].

The FTIR collects IR scans every 1.5 seconds. It was set to calculate and collect molar fraction after 8 scans - every 12 seconds. The molar fractions used in our calculations were therefore average of 8 values collected by the FTIR. The shortest time of reaching 5 % of the input molar fraction was 1040 seconds (0.2 MPa, x_{CO} = 0.00051), so the capacity that we calculated is a sum of 88 approximations. Other calculated capacities are sums of higher number of approximations.

Our results indicate that increasing pressure increases oxidative capacity. This could be caused by increased partial pressure while the molar fraction of carbon monoxide remains the same. More experiments need to be carried out in order to confirm this assumption. However, this phenomenon can be supported by Lee and Kim [12] and also by Avgouropoulos and Ioannides [11] who state, that the CO oxidation rate is dependent on the partial pressures of CO, CO_2 and H_2O.
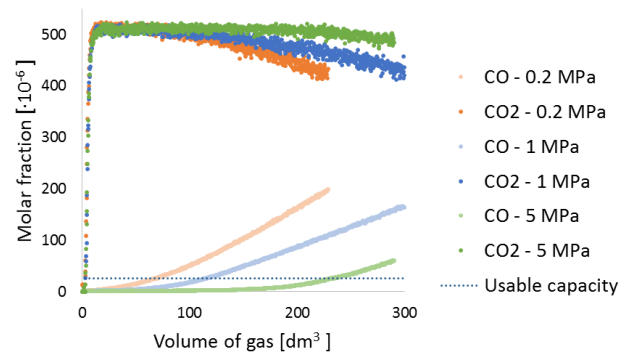The calculated capacities are lower than proposed 50% efficiency of the conversion [8].

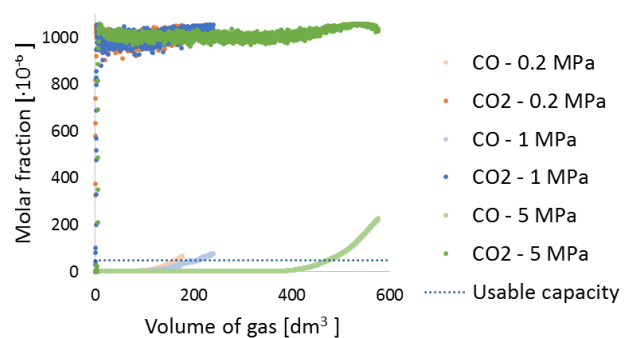**Figure 5** Breakthrough curves of helium gas mixture (x_{CO} = 0.000510)

Figure 6 Breakthrough curves of helium gas mixture (x_{CO} = 0.000510)

This may be caused by low layer of CuO in the heated column or by high gas flowrate that results in short delay time.

Line analysis conducted on used CuO particle cut is shown in Fig. 7. Results of the analysis show that copper and oxygen dominate in the particle composition. Oxygen content oscillate in the depth of 150 µm from the particle surface around 25 % wt. More significant changes in oxygen content occur in the less homogeneous area of the particle shown in Fig. 7. Contrary to our assumptions, no significant decrease in oxygen content was observed near the particle surface. For comparison, an analysis of unused particle was carried out. Detected content of carbon, copper and oxygen was very similar to the composition of used particle. The results of SEM-EDX analysis do not demonstrate no difference in elemental composition of the near-surface area and deeper areas of CuO particles and no difference in composition of used and unused particle.

Tab. 2 Calculated oxidation capacities of CuO for CO conversion under various conditions

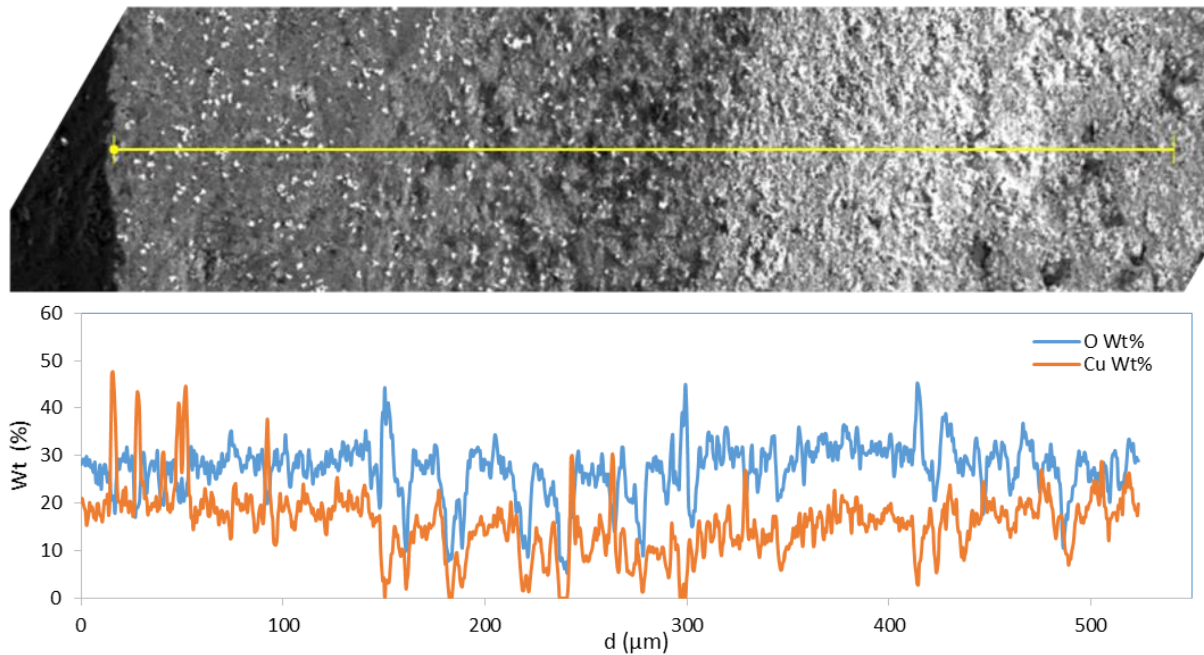| x_{CO}	Flowrate (dm³·min⁻¹)	m_{CuO} (g)	Pressure (MPa)	Capacity ($g_{CO} \cdot g_{CuO}^{-1}$)	Capacity ($n_{CO} \cdot n_{CuO}^{-1}$)
993 · 10⁻⁶		4.79	0.2	0.036	0.10
		4.94	1.0	0.044	0.12
		4.98	5.0	0.100	0.30
	1	2.10	0.2	0.017	0.05
510 · 10⁻⁶		2.11	1.0	0.028	0.08
		2.01	5.0	0.060	0.17

Figure 7 Line SEM-EDX analysis of a polished cross-cut of used CuO particle. Surface of the particle is on the left side of the figure.

4. Conclusions

Experiments were performed on the laboratory scale apparatus to obtain oxidation capacity CuO for CO conversion. Our calculated sorption capacities (0.05 – 0.3 conversion) are lower than capacities used in literature (0.5 conversion). This may be caused by short CO delay time in the heated column. Further experiments with different volume fractions of CO in helium need to be performed in order to create a mathematical model for simulations with different volume fractions. SEM-EDX analysis did not show no structural difference in used and unused CuO particle.

Acknowledgements

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