INTRODUCTION
Natural gas hydrates are ice-like solid compounds, characterized by a crystalline structure based on water molecules, which contains natural gas molecules [1]. From their discovery in 1778, the history of gas hydrates addressed three different periods. At the beginning, hydrates were mainly considered a scientific curiosity. Starting from 1934, due to their ability in causing gas pipelines blockage, gas hydrates started being investigated with the aim of avoiding their formation and preventing the related issues for the natural gas industries. The third period started in the mid-1960, when hydrates started to be considered as a new promising energy source. In those years, the first natural deposits were discovered and the first estimations about natural gas quantities present worldwide under form of hydrate were made. To date, the quantity of natural gas contained into hydrates is estimated to be enough to produce more than twice the energy that can still be obtained from all conventional energy sources put together [2-4]. Those reservoirs are mainly sited in permafrost regions (about 3%) and in marine sediments (the remaining 97%). The most abundant reservoirs were found in the South China Sea, Japan Sea, Indian Ocean, Gulf of Mexico, Bering Strait and Seas of Korea [5]. The growing interest on natural gas hydrates is also due to the possibility of making them a carbon neutral energy source, due to the possibility of directly replacing methane with an equal number of carbon dioxide molecules. Unfortunately, the exploitation of hydrates reservoirs is nowadays far from being attractive for industrial large-scale applications, because of economic and environmental challenges. In fact, hydrate compounds act as solid skeleton of frame sediments and cement sediment particles [6, 7]. When methane is recovered from hydrates, water cages inevitably dissociate, whit the following loss of shear strength and instability of the well [8-11]. Currently, economic issues represent the most limiting factor; intervening on hydrates reservoirs means address problems related to the extremely elevated depths, difficulties in gas diffusion through adjacent hydrate layers, methane hydrates re-formation and so on. The main techniques to act on hydrates reservoirs are based on depressurization [12, 13], thermal stimulation [14, 15] and chemical inhibitor injection [16]. Depressurization and thermal stimulation strategies are based on varying the local thermodynamic conditions, in order to make them unfeasible for hydrates stability [17, 18]. Conversely, chemical inhibitors are used to shift the equilibrium of hydrates to higher pressures or lower temperatures, thus preventing the related issues for the natural gas industries. The present work describes gas hydrates formation in a small-scale reactor, filled with water and pure quartz sand and with the addition of a metallic CuSn12 powder, which can be found as residual products in steel plants coming from steel making.

ABSTRACT
Natural gas hydrate represents one of the most promising solutions to answer to the constantly increasing energy demand; in addition, the possibility of recover methane via carbon dioxide injection, with a theoretical exchange ratio equal to 1, makes it a potential carbon neutral energy source, which might act as leading parameter toward an energetic scenario completely dominated by renewable energy sources. However, some topic issue needs to be solved to make such resource feasible for large-scale industrial applications. Among them, energetical costs associated to practical operations in marine deposits. The use of chemical inhibitors and or promoters to improve the exchange process is gaining increasing interest and researchers are mainly focused on finding less environmental unfriendly additives and on reducing their costs. In that direction, the present work deals with the possible use of waste dust, produced during steel mill processes, as promoter of the CO2/CH4 replacement process. Those sands commonlly contain a great variety of compounds, such as metal oxides, alumina, salts, and so on. Some of them have a chemical composition close to well-known hydrate inhibitors/promoters. Moreover, those wastes, otherwise destined for landfill disposal, could find application as starting materials for further innovative energetic cycle. In this work, both methane and carbon dioxide hydrate formation were tested in absence and in presence of cupper oxides, with different concentrations. Hydrate formation and dissociation results where then compared among each other and with hydrate equilibrium values for those compounds, previously verified and available elsewhere in literature.

Keywords: steel plant; circular economy; cupper oxides; waste dust utilization; CO2 capture.
process in case of ladle furnace. This is particularly true in case of production of high strength steels (which requires for heavier micro-alloying) [19,22]. The study is included in wider research, which deals with the experimental definition of the technical feasibility of using metallic powders, realized via gas atomization and commonly destined to additive manufacturing applications, as potential additives capable to improve the CO2/CH4 exchange efficiency during replacement processes in natural gas hydrate reservoirs [23-26]. The goal is to simulate, with these powders, the possible usage of residual dust from steel mill processes. Two guest compounds were used, or methane and carbon dioxide. The aim of this experimental campaign, was to establish if that metallic powder was able to intervene on the hydrate formation process, thus promoting or inhibiting it. To do this, hydrates were firstly formed without this powder, then it was added to the porous medium and experiments were repeated again. Hydrates were firstly formed and then dissociated; in this way, it was possible to draw the equilibrium curve for both components. Results were then compared with how present in literature about equilibrium for methane and carbon dioxide hydrates. Moreover, in order to improve the gas storage efficiency and increasing the energy density per unit of volume, it is foreseen the possibility to realize tanks and cylinders with an 3D-printed internal high-porous metallic lattice. The feasibility of such strategy might be improved, in the next future, by using residual dust from steel mill processes to realize the tanks as soon mentioned.

MATERIAL AND METHODS

Experimental apparatus

The lab-scale experimental apparatus used in this work, has been previously tested in recent experimental campaigns and a detailed description of it is available elsewhere in literature [27-29] The reactor was completely made with 316SS and as an internal cylindrical volume equal to 949 cm³ (Figure 1). It is inserted in a thermostatic bath, used to control the internal temperature. Four Type K thermocouples and a digital manometer were used to measure the thermodynamic condition inside the reactor. Gas injection occurred from the bottom, in order to promote, as much as possible, gas diffusion into sand pores. Conversely, gas ejection was performed from the top. Figure 1 shows a scheme of the completely assembled experimental apparatus.

All devices were connected to the LabView software, with a data acquisition system manufactured by National Instrument and used for monitoring and recording data from sensors.

Fig. 1 Scheme of the completely assembled experimental apparatus.

Materials

Ultra-High Purity (UHP) methane and carbon dioxide were used, with a purity degree respectively equal to 99.97% and 99.99%. Sand consists of pure quartz spheres, having diameter equal to 100 µm. The average porosity of sand was measured with a porosimeter, model Thermo Scientific Pascal 140, and is equal to 34%. The reactor was filled with 744 cm³ of sand and 236 cm³ of water. Considering the porosity of sand, the remaining free space was used for gas injection.

The metallic copper-tin powder (CuSn12), used in this work, was produced with the gas-atomization technique. These kinds of raw materials are commonly produced for applications in additive manufacturing [30-34]. The alloy nominal chemical composition, expressed in weight%, is 12% Sn and 88% Cu. High-resolution electronic scanning microscope (FE-SEM Zeiss LEO-1530), was used to analyze the morphology of the present powder. The shape of grains is mainly spherical, with a size ranging from 5 µm to 20 µm. The powder morphology is shown in Figure 2.

Fig. 2 Powders morphology of CuSn12 alloy, SEM images.

The internal temperature was kept to 1-3 °C. Gas injection occurred slowly and pressure increased with a constant gradient. The initial pressure was fixed at 54 – 56 bar in presence of methane, while 38 – 40 bar were established in tests with carbon dioxide. Once feasible values of pressure and temperature were reached, the reaction started, with a sudden slow decrease in pressure. Initially temperature increased significantly, because of the exothermicity of hydrates formation; then it decreased again and reached the thermal balance with the experimental apparatus. As soon as pressure stabilized, the process finished. Immediately after, the chiller was switched-off and temperature increased. The following dissociation of formed hydrates was used to define the equilibrium curve for methane and carbon dioxide hydrates, both in absence and in presence of CuSn12 powder.

Methods

The porous medium was used to ensure a massive hydrates formation in the whole internal volume of the reactor and not only in the portion close to the gas-liquid interface. Moreover, sand allowed to well distribute the powder along the whole reactor. Two experiments were carried out without the CuSn12 powder, while other two tests were made with 500 g of it, which corresponds to 30.66 wt.%. The powder was firstly mixed with silica sand; the mixture was then inserted in the reactor, together with water. The mixture of sand and powder is shown in Figure 3.

Fig. 3 Quartz sand and CuSn12 powder before mixing them (a) and after (b).
The internal temperature was kept to 1-3 °C. Gas injection occurred slowly and pressure increased with a constant gradient. The initial pressure was fixed at 54 – 56 bar in presence of methane, while 38 – 40 bar were established in tests with carbon dioxide. Once feasible values of pressure and temperature were reached, the reaction started, with a sudden slow decrease in pressure. Initially temperature increased significantly, because of the exothermicity of hydrates formation; then it decreased again and reached the thermal balance with the experimental apparatus. As soon as pressure stabilized, the process finished. Immediately after, the chiller was switched-off and temperature increased. The following dissociation of formed hydrates was used to define the equilibrium curve for methane and carbon dioxide hydrates, both in absence and in presence of CuSn12 powder.

RESULTS AND DISCUSSION

This section has been divided in two main parts: tests involving methane and tests involving carbon dioxide. All experiments were represented in a pressure-temperature diagram. Finally, results were put together and compared, in order to verify if this specific sand affected the process or not and also to determine if it produced similar effects in both cases or not.

Methane hydrates formation
Equilibrium values, obtained for methane hydrates, both in presence and in absence of the CuSn12 powder, are reported in Figure 4 and Figure 5.

Carbon dioxide hydrates formation
Equilibrium values, obtained for carbon dioxide hydrates, both in presence and in absence of the CuSn12 powder, are reported in Figure 6 and Figure 7.

Direct comparison between results reached with the two different guests
In this section, hydrates equilibrium values, obtained in the previous experiments, were put together and compared with data taken from literature [35–41]. Results were shown in Figure 8.

In the figure, the two dotted lines were used to indicate the ideal methane and carbon dioxide hydrates equilibrium, based in values present elsewhere in literature. Tests involving methane were shown with “warm” colors, while tests made with carbon dioxide with “cold” colors. In absence of powder, methane hydrates formed at milder conditions than that commonly required for the process (red line), while the opposite occurred for carbon dioxide hydrates (blue line), whose formation required more severe conditions than for pure methane, at temperatures below 5 °C. The addition of the metallic powder to the porous medium, clearly promoted the process. At low temperature values, any variation occurred for methane hydrates; conversely, with the increase of temperature, methane hydrates formed at lower pressure values if compared with what required in absence of powder. The effect was till more significant for carbon dioxide hydrates; the addition of the CuSn12 powder moved the equilibrium curve below the equilibrium line and the formation trend was very similar to the ideal one.

Based on these results, this powder can be used for gas storage; in particular, with appropriate treatments, such powder or similar ones, might be used to build a metallic high-porous lattice, able to improve the promoting effect proved in these experiments.
This article deals with methane and carbon dioxide hydrates formation in presence of a pure quartz porous sand and a powder made with CuSn12 metallic alloy. Topic of experiments carried out in this work, was to establish if this specific powder intervenes on the hydrates formation process or not and, in the first case, if its effect consists in inhibiting or promoting the formation. A small-scale experimental reactor was used to perform the process and four experiments were made. For both compounds, hydrates were produced with the only presence of quartz sand and with the addition of the CuSn12 powder, with a concentration equal to 30.66 wt.%. Experiments led to a promotion of hydrates formation, both when methane or carbon dioxide were used. The effect was more pronounced in presence of this latter compound: the promoting action was found to be more effective when methane or carbon dioxide were used. The effect was only presence of quartz sand and with the CuSn12 powder, with a concentration equal to 30.66 wt.%

CONCLUSIONS

This article deals with methane and carbon dioxide hydrates formation in presence of a pure quartz porous sand and a powder made with CuSn12 metallic alloy. Topic of experiments carried out in this work, was to establish if this specific powder intervenes on the hydrates formation process or not and, in the first case, if its effect consists in inhibiting or promoting the formation. A small-scale experimental reactor was used to perform the process and four experiments were made. For both compounds, hydrates were produced with the only presence of quartz sand and with the addition of the CuSn12 powder, with a concentration equal to 30.66 wt.%. Experiments led to a promotion of hydrates formation, both when methane or carbon dioxide were used. The effect was more pronounced in presence of this latter compound: the addition of powder moved the equilibrium curve below the ideal curve, produced with data present in literature. About methane, the promoting action was found to be more effective with increasing temperatures.

REFERENCES


DOI: 10.36547/ams.28.4.1632

206