CO$_2$ Hydrates as a climate change mitigation strategy: Definition of stability zones in the Portuguese deep offshore

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Abstract — Storage of CO$_2$ as hydrates in sub-seabed sediments has been pointed out as an alternative solution for the geological storage of CO$_2$, particularly suitable for offshore areas where large ocean depths and low temperatures are reached at short distance from the onshore. This is the case for Portugal, where the continental shelf can be as narrow as 10 km. This paper presents the works conducted to identify the CO$_2$ Hydrates Stability Zone, i.e. the areas where CO$_2$ hydrates may form and remain stable, in the deep offshore of Portugal. The methodology adopted involved building maps of geothermal gradient, temperature of water, detailed bathymetry and conversion to hydrostatic pressure, and maps of sediment thickness. These maps were integrated in a GIS environment and a Fortran code was implemented to compute the thickness of the Hydrate Stability Zone, based on the pressure and the temperature conditions on the sub-seabed sediments. Preferential areas, where further studies should be conducted, were defined based on thickness and thickness variation of the Stability Zone, depth of the water column and distance from the main harbours.

Keywords — CO$_2$ hydrates, CO$_2$ storage, Portugal, sub-seabed sediments

1 INTRODUCTION

The IPCC 4th Assessment Report [1] stated as highly likely that anthropogenic activities are the main cause of ongoing climate change. Climate change is linked to the concentration of greenhouse gases (GHG) in the atmosphere, which have been increasing since the industrial revolution. The most important of those GHGs is carbon dioxide (CO$_2$), which has been emitted to the atmosphere in large quantities, mainly due to the burning of fossils fuels.

Carbon Capture and Storage (CCS), a process in which CO$_2$ is captured in large stationary sources and permanently stored in deep geological formations, is pointed as one of the technologies that can be used to minimise climate change. The main stationary sources where CO$_2$ could be captured are power plants, refineries, cement plants and steel mills.

As for geological storage, several possibilities have been studied in recent years. Deep saline aquifers, depleted hydrocarbon fields, unminable coal seams and Enhanced Oil Recovery are the sinks most likely to be implemented in the near future [2]. Although at an earlier stage of development, other forms of geological storage have been the subject of research. One of them is the injection of CO$_2$ in sub-seabed sediments as clathrates or hydrates [3], [4].

Hydrates are characterised by non-stoichiometric crystalline structures formed by water molecules and gas molecules under certain temperature and pressure conditions. If those conditions are the right ones, several water molecules form a cage surrounding one gas molecule (Fig.1). This mechanism can traps CO$_2$ (as well as other gases) in an "ice-like" form rendering it immobile.

Storing CO$_2$ as hydrates in sub-seabed sediments consists on the injection of slightly buoyant liquid CO$_2$ below the depth where hydrates would form. Being less dense than the formation water, the CO$_2$ rises and eventually forms hydrates that provide a cap for liquid-form CO$_2$ stored at higher depths.

The process of forming CO$_2$ hydrates requires low pressures and temperatures that are usually found in permafrost environments or at large depths within the ocean.
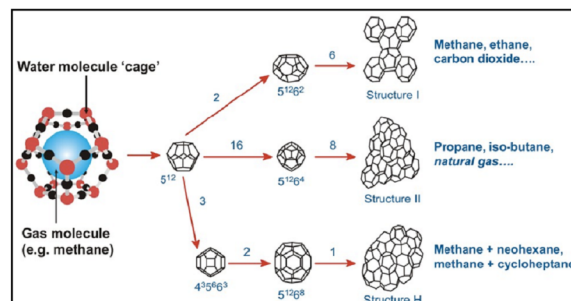

Fig. 1. Structures of clathrate hydrates. Adapted from Sloan [5].

A previous work by Rochelle *et al.* [4] mapped the areas in NW Atlantic where CO$_2$ hydrates could form and be stable. The offshore Portugal was pointed out as having potential for CO$_2$ storage as

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hydrate in sub-seabed sediments. The work by Rochelle *et al.* [4] relied on generic information about the pressure and temperature. The aim of this paper is to define the hydrate stability zone in the Portuguese deep offshore, resorting mainly to the data gathered in the works carried out in the application for the extension of the continental shelf (submitted to the UN in 2009).

2 BACKGROUND

Storing CO_2 in deep-sea sedimentary strata was first proposed by Koide *et al.* [7], [8] and are based on the concept that CO_2 hydrates stability conditions are similar to methane (CH4) hydrates. If natural CH4 hydrates occur and remain stable in sub-seabed sediments, then it should be possible to store CO_2 in the same form and in the same environment.

Thermodynamic calculations show that CO_2 hydrates are stable at relatively low-pressure (low water depths) conditions at a typical seabed temperature. The required conditions vary usually from 0 °C to 7 °C and from 1 MPa to 30 MPa. For very high pressures (depths above 3000 m) CO_2 has a higher density than the surrounding water, providing gravitational stability and preventing diffusion or escaping processes [9].

The process of storing CO_2 in hydrate form involves injecting CO_2 in the deep-sea cold sedimentary strata. The injected liquid CO_2 extends horizontally in the sediments, and flows upward to the generation of CO_2 hydrate creating a self-sealing cap. A large volume of CO_2 can be further sequestered under this cap or the cap can act aa secondary seal for subsurface storage sites (e.g., depleted reservoirs and/or saline aquifers) [10], [11] (Fig.2).
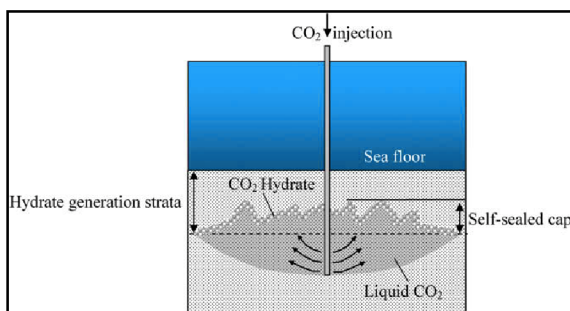

Fig. 2. Scheme of CO_2 injection and hydrates formation. Adapted from Li Q *et al.* [11]

Resorting to seabed temperature and pressures, and to geothermal gradient, it is possible to define a Hydrate Stability Zone (HSZ) resulting from the intersection of the hydrate phase boundary and the temperature-depth profiles imposed by the hydrothermal and geothermal gradient (Fig.3.).
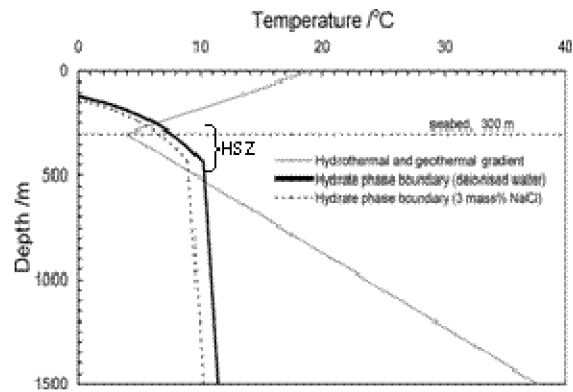

Fig. 3. Example of predicted Hydrate Stability Zone (HSZ) for CO_2 hydrates formed in the presence of fresh water and saline water. The upper and lower limits of the HSZ are given by the intersection of the hydrate phase boundary and the temperature-depth profiles imposed by the hydrothermal and geothermal gradient. Adapted from Tohidi, Yang *et al.* [10].

Rochelle *et al.*, 2009 [4] mapped the HSZ thickness in the NW Atlantic using a hydrate phase boundary given by:

$$\ln P = A - B/T \qquad (1)$$

where P and T represent the dissociation pressure and temperature, respectively, and A and B are empirical constants found by linear correlation to the results of the CSMHYD code [5], that computes the thermodynamics of stable hydrate structures. A temperature offset of 11. °C was considered to compensate for decreased hydrate stability due to salinity effects.

The results presented in this paper complement those of Rochelle *et al.*, 2009 [4] in which specific information on geothermal gradient, sea water temperature and existing sediment thickness are used, and a different approximation to the CO_2 hydrate phase boundary is used, which considers the inhibitor effect imposed by water salinity.

3 METHODOLOGY

To define the stability areas a Geographic Information Systems (GIS) was implemented, gathering the data on the relevant features of the deep offshore, while the calculations were implemented in a Fortran code.

The GIS includes data on bathymetry, hydrostatic pressure, temperature at the bottom of water column, oil exploration drilling wells, geothermal gradient, sediment thickness, the main CO_2 stationary sources in Portugal and the main Portuguese harbours.

The definition of the HSZ was computed using the following procedure:

1. Build raster datasets of geothermal gradient, seabed temperatures, hydrostatic pressure and sediment thickness in the study zone;

2. Establishment of CO_2 hydrates phase boundary equation as an approximation to the results of CSMHYD [5];
3. Implementation of the phase boundary equation calculated in 2. on a Fortran code;
4. Using the Fortran code, verification of the CO_2 hydrates stability at seabed, using the seabed pressure and temperature rasters. The results are the offshore areas where CO_2 hydrates are stable;
5. For the areas in 4, the geothermal gradient, hydrostatic pressure and sea-bottom temperature rasters are combined to find the depth in sub-sea bed sediments where hydrates are no longer stable, e.g. the depth to the lower limit of the HSZ and, correspondingly, the HSZ thickness (Fig. 3);
6. Intersection of the HSZ raster defined in 5. with the raster of existing sediment thickness, resulting in the final HSZ thickness.

4 STUDY AREA AND DATASETS

The study area is bounded to the East by the Portuguese coast or by the limit of the Portuguese Economic Zone, to the North and South by the limit of the Exclusive Economic Zone and extends to the West to approximately 200 nautical miles from the coast (Fig. 4).

4.1 Geothermal Gradient

There was no established map of geothermal gradient in the deep offshore of Portugal, so a compilation of data was made from unpublished reports [12], from Bottom-Hole Temperatures (BHT) in oil exploration wells and from the Integrated Deep Ocean Drilling Program (IODP). Corrections of the BHT were done using standard methodologies [13] and geothermal gradients were calculated taking into account the temperature at sea-bottom. Data from heat flow in oil and mining exploration wells were also used, as listed in the Atlas of European Geothermal Resources [14].

The amount and distribution of data is far from desirable, but it was possible to build the geothermal gradient map depicted in Fig.4.

4.2 Seabed temperature

Water temperature was downloaded from National Oceanographic Data Center (NODC) internet site [15] and reflects temperature measurements made in the water column with a Conductivity Temperature Depth (CTD) profiler. Temperature was measured at several depths, not necessarily coinciding with the sea-bed. Linear regression was used to extrapolate from the deeper temperature to the sea-bed. Fig.5 depicts the sea-bed temperature map produced.
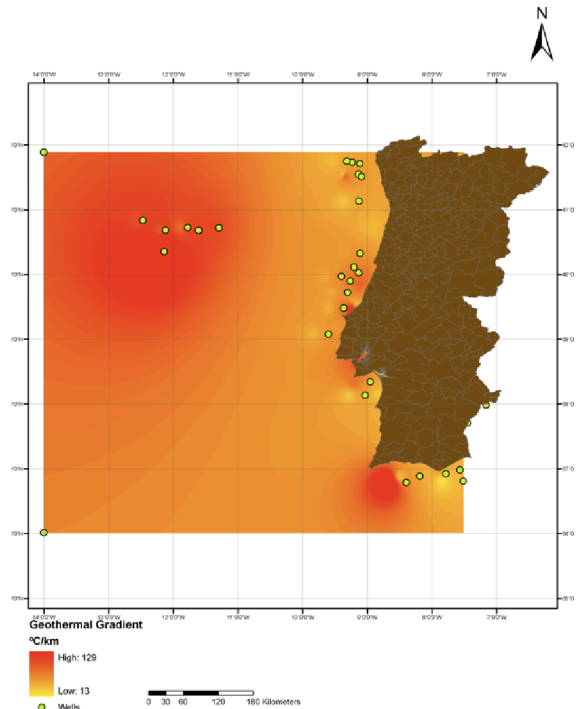

Fig. 4. Geothermal gradient map. Dots represent the wells where geothermal gradient was estimated.
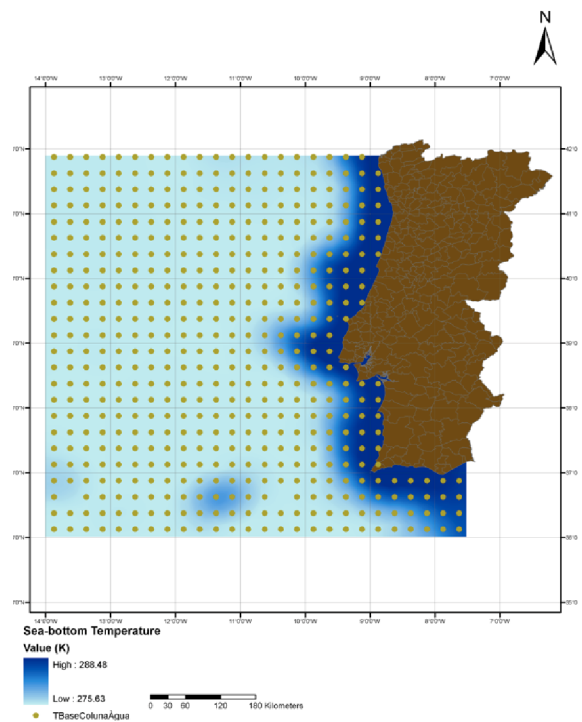

Fig. 5. Seabed temperature map. Dots represent the water temperature grid from NODC site.

4.3 Hydrostatic pressure

The raster of the hydrostatic pressure at the seabed was built using the bathymetry acquired by EMAM, the Task Force for Maritime Affairs, using a high resolution multi-beam system. A constant seawater

density value was used (1027 kg/m^3). Fig.6a shows the bathymetric map, while Fig.6b shows its conversion to pressure.
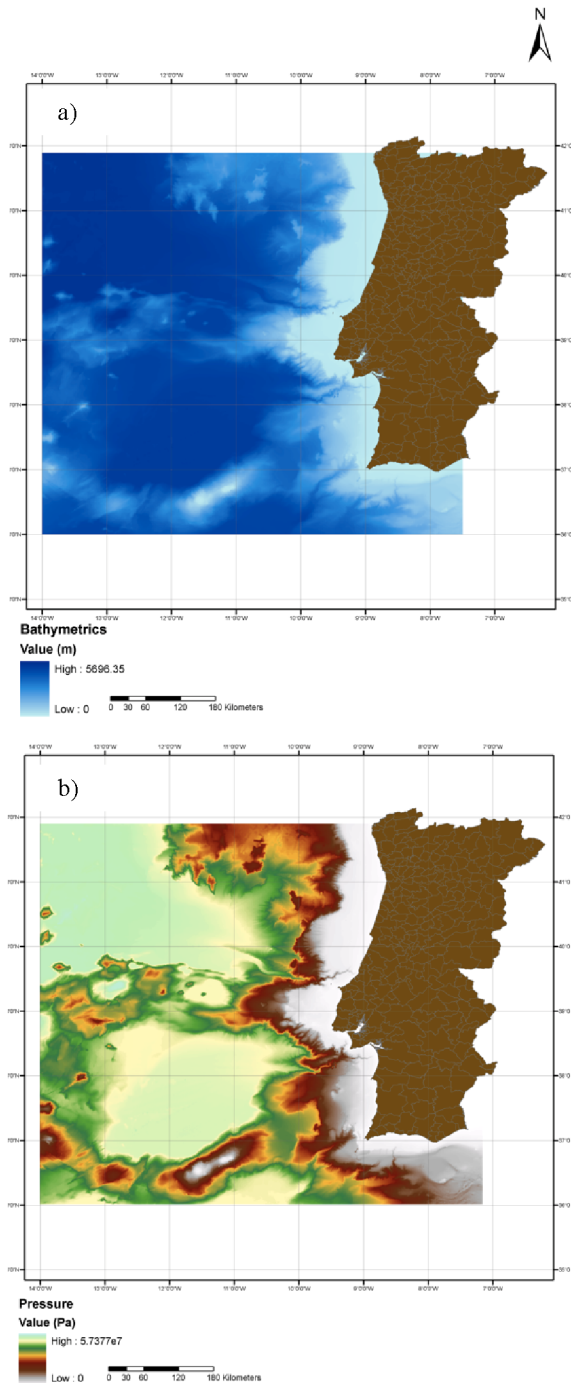

Fig. 6. a) Bathymetry; b) Pressure (Pa) at seabed.

4.4 Sediment thickness

The source of information used for the existing sediment thickness was the National Oceanic and Atmosphere Administration (NOAA) which mapped the sediment thickness in the North Atlantic with a resolution of 0.05x0.05 degrees [15]. Fig.7. shows the sediment thickness in the study area.
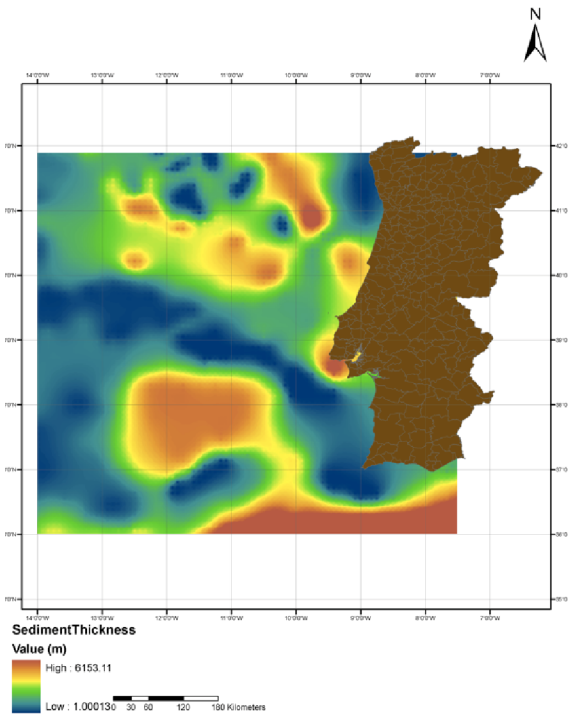

Fig.7. Sediment thickness map.

4.5 Approximation to the hydrate phase boundary

The definition of the HSZ needs to take into account the takes into account the thermodynamics of the hydrate phase boundary, including pressure and temperature variations, as well as the inhibitor effect of the formation water salinity.

Since the equation describing that complex thermodynamic behaviour is difficult to implement and work in conjunction with the GIS, an approximation to the phase boundary computed by the CSMHYD [5] code was used, taking into account a seawater salinity of 36 g/l as an inhibitor. Pressure and temperature dissociation pairs were found in CSMHYD and using a non-linear regression the following function was adjusted:

$$\frac{1}{T} = \sum_{i=1}^{4} b_i \left(\ln P_d \right)^{i-1} \qquad (2)$$

where T_d and P_d are the dissociation temperature and pressure, respectively and b_i are the constants b_1=9.59x10^{-3}, b_2=-1.85x10^{-3}, b_3=1.9x10^{-4} and b_4=-6.58x10^{-6}. Fig.8 shows the fit of this function to the CSMHYD data. This equation is very similar to the one given by Carrol *et al.* [16] for ethane hydrates.
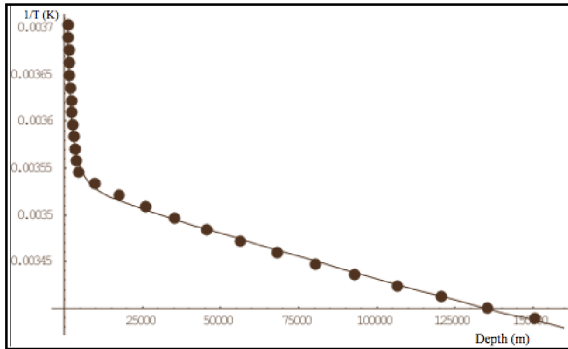
Fig. 8. Non-linear regression fit of equation (2) to CSMHYD data.

Converting the pressures in equation (2) into depths and plotting against seabed temperature measurements it is possible to conclude that in the Portuguese deep offshore, hydrates will not form at depths lower than 1100 m (Fig.9). This is in sharp contrast with other studies that point towards hydrate formation at depths as lower as 400m and is an effect of the warmer water currents in the study area.

5 RESULTS

Equation (2) was implemented in a Fortran code - *CO2Hydrate* - to perform the computations using the GIS raster grids as input.

CO2Hydrate computes if each raster cell is above or below the phase boundary indicated (equation (29 and Fig.8), i.e. if the hydrates are stable, or not, resulting in the hydrates stability zones depicted in Fig.10. Notice that even though hydrates form at deep waters, the edge of stability zone is less than 50 km away from portuguese coast.
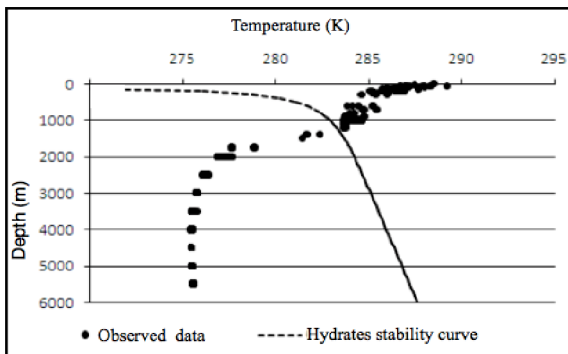

Fig. 9. Seabed temperature (K) measurements and hydrate phase boundary, against water depth, showing that hydrates are stable only for water depths above 1100 m.

To define the thickness of the HSZ (e.g., the depth below the seabed where the CO_2 hydrates are no longer stable) *CO2Hydrate* computes the pressure increase and the temperature increase with depth due to the geothermal gradient according to:

$$T = T_0 + \frac{dT}{dz}Z \qquad (3)$$

where T is the temperature value at depth Z, T_0 is the temperature at a reference depth (seabed) and dT/dz is the geothermal gradient value. *CO2Hydrate* finds the value of Z at which the hydrates are no longer stable by numerical inversion of the equality between equations (2) and (3).
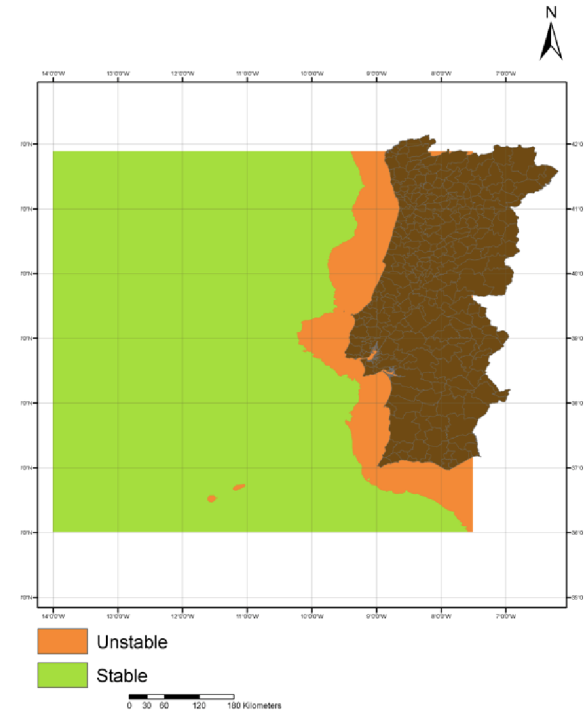

Fig. 10. CO_2 hydrates stability zone in the deep offshore of Portugal.

The HSZ thickness thus computed is then checked against the existing sediment thickness in each raster cell. The smallest of the two values is adopted has the final HSZ thickness. Fig. 11 shows the HSZ thickness map. The maximum thickness found is 382 meters.

6 DISCUSSION

The hydrate stability zone extends for a large area in the Portuguese deep-offshore. Although, theoretically any location in such area could be suitable for storing CO_2, in practice it is necessary to take into account the distance to Portugal's mainland and differences that may exist in terms of safety.

In order to further restrict the area where further studies should be conducted, four other factors were considered, based on storage security and economic:
I. HSZ Thickness - higher thickness implies more confidence on the trapping mechanism;
II. Variation of HSZ thickness - smaller variation increases safety;
III. Depth of the water column - higher depths imply increased costs for storage;
IV. Distance to Portugal's main harbours -

higher distances imply higher costs.

The HZS thickness raster (Fig.11.) and the bathymetry raster (Fig.6a.) were reclassified from 1 (poor) to 10 (excellent) to account for the criteria in I. and III.
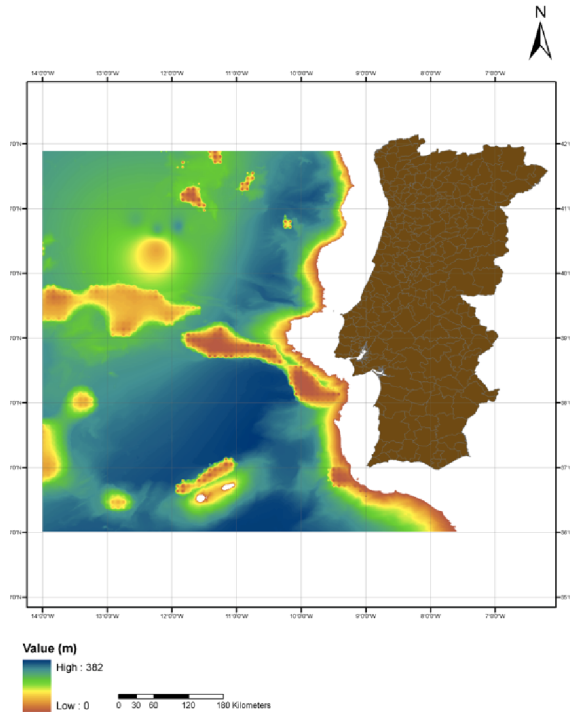

Fig. 11. Thickness (m) of the Hydrate Stability Zone.

Rasters of HZS thickness variation and distance from every cell to the nearest of the four main harbours in Portugal were built and reclassified in the same manner.

After the reclassification process, the factors were weighted and added according to:

$$A = \sum_i P_i X_i \qquad (4)$$

where A represents the ranking index and P represents the weight given to each four factors X. The weights were defined, arbitrarily, as: HSZ thickness - 0.35; depth of water column - 0.25; variation of HZS thickness - 0.15 and distance to main harbours - 0.25.

The A ranking factor calculated for the entire study area is mapped in Fig.12. No areas scored above A = 8 (10 was the maximum possible). Areas with a ranking factor A>6.5 are shown in Fig.13, showing that some of the highest ranking areas are located less than 40 Nautical Miles from Portugal's mainland. These are considered to be the most interesting areas, where further studies should be made.
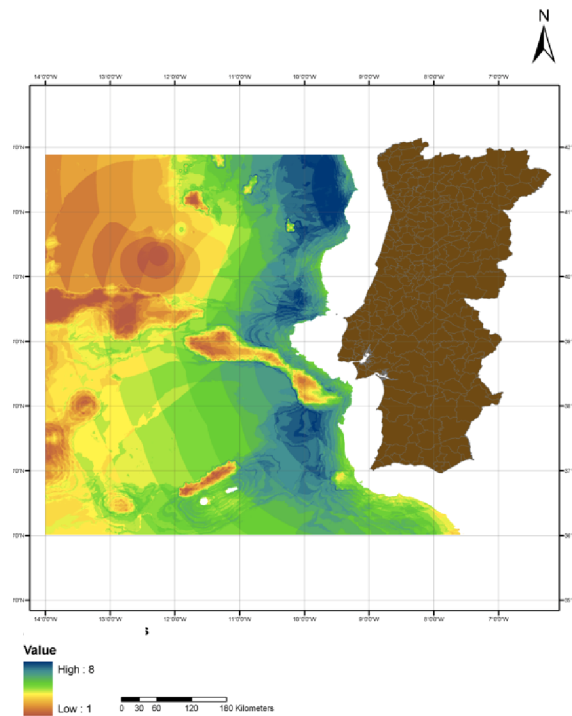

Fig. 12. Ranking factor for the CO₂ hydrate stability zone.

7 CONCLUSIONS

Storing CO₂ in hydrate form in sub-seabed sediments has the potential for being an interesting solution for reducing CO₂ emissions in countries where the continental shelf reaches high depths close to seashore.

This is the case of Portugal, where the shallow offshore (bathymetry > - 200 m) is in some areas less than 10 km wide.

This paper is a first effort towards defining the hydrate stability zones in the deep offshore of Portugal.

A GIS was implemented to gather data on the bathymetry, pressure, seabed temperature and sediment thickness. A new geothermal gradient map was produced and also incorporated in the GIS.

A non-linear approximation to the CO₂ hydrate phase boundary was adjusted and implemented in a computer code to delineate areas where the hydrates are stable and to compute the thickness of the stability zone.

The warm currents in the Portuguese offshore area indicate that CO₂ hydrates are stable only for deep waters, more than 1100 m of water column. The stability zone is considerably large in area, and shows a thickness up to 382 m.
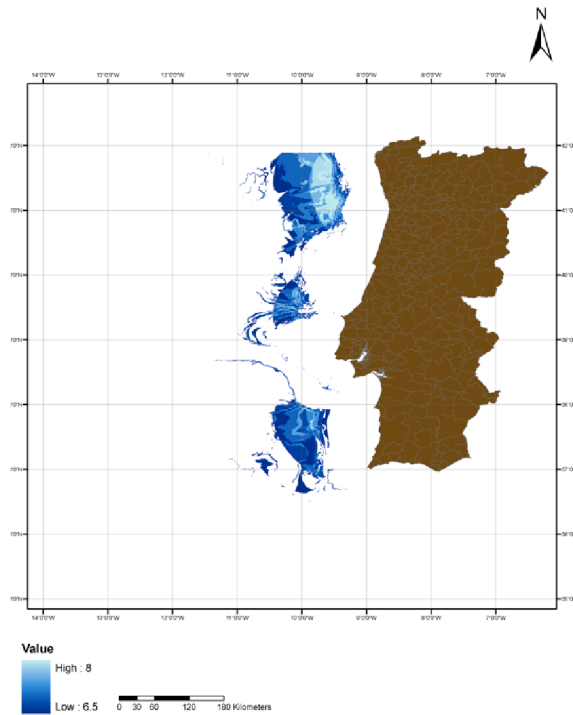
Fig. 13. Areas with a ranking factor A>6.5. Red dots represent maritime harbors, white dots represent the CO₂stationary sources with emissions > 0.1 Mt/year.

To further rank the stability zone, a weighted procedure was implemented, considering economic and safety factors, namely: water column depth, distance to main harbors, HSZ thickness and variation of HZS thickness. This methodology resulted in the delineation of the areas where further studies should be conducted.

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