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آموزش مهارت های کاربردی در تدوین و چاپ مقاله

CO₂ STORAGE MECHANISMS AND METHODS: A SURVEY STUDY

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ABSTRACT

Nowadays, the accumulation of greenhouse gases (e.g. water vapor, carbon dioxide, etc.), which are produced by human activities has become one of the most serious environmental problems. Climate change and man-made global warming as a result of the growth of carbon dioxide (CO₂) concentrations in the atmosphere is one of the main human concerns about the health and environment. In order to diminish negative impacts of global warming, it is essential to reduce CO₂ emission by using effective and feasible methods. One way to reduce greenhouse gases (GHGs) emissions is through reducing consumption of fossil fuels; however, such decision may negatively impact the economy. Another option, which may be the more effective action, is to reduce the CO₂ concentrations through geological storage. For this purpose CO₂ should be captured, transferred and injected in an appropriate geological structure, which can securely store CO₂ for a long period of time.

In this literature survey study, CO₂ storage methods and its trapping mechanisms are discussed in details. After introducing different promising media for storage, the necessity and the opportunities of geological storage of CO₂ in Iran are discussed.

INTRODUCTION

Carbon dioxide capture and storage (CCS) is a well-established method to reduce the CO₂ concentration of the atmosphere. This process includes three steps; the first step is to capture CO₂ from major sources such as power plants. The second step is to transport the captured CO₂ to the storage sites via pipelines or ships. Finally, it should be injected into a suitable place such as a geological formation.

Carbon dioxide can be stored in different places such as depleted gas and oil fields, saline formations, coal seams, basalts, gas or oil shales, salt caverns, abandonment mines and oceans [1]. Storage in all of

the above-mentioned places excluding the last one is known as underground geological methods. It has been practically shown that storage processes could be performed in some of these places such as depleted hydrocarbon reservoirs and saline formations.

Past successful gas storage projects, suggest that CO₂ could be rapidly injected and securely stored for a long time at suitable underground places [2-4]. It is considered, that about 99% of the injected CO₂ would be retained after 1000 years [1]. The two essential criteria for selecting a proper storage site are having a considerable storage capacity and a safe sealing to prevent leakage [5].

Density of CO₂ increases with depth [6, 7]. Storage is more effective at depths below at which (800-1000 m); CO₂ becomes supercritical and has a liquid-like density (Figure 1). At this condition the storage capacity increases. Density change also depends on CO₂ stream composition and temperature gradient of formation. Cold sedimentary formations (with low temperature gradient) in which CO₂ has higher density at the same depth compared to warm basins, are more favorable sites for storage purposes [7].

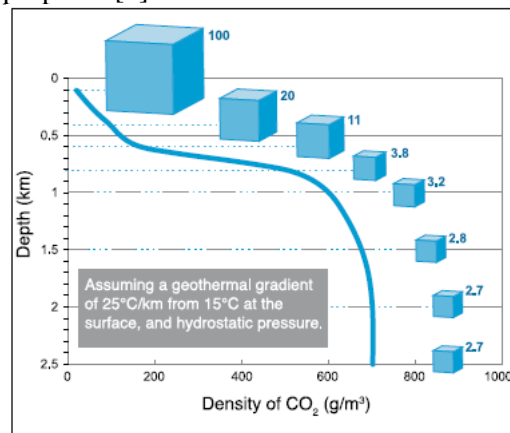


Figure 1
Variation of CO₂ density with depth, [8].

In this paper, different geological storage sites and trapping mechanisms are first explained; and then the possible places for CO₂ storage are discussed. At the last section of this study, based on some statistical data of CO₂ emission, the requirements for CO₂ storage in Iran are being mentioned, and then formations, which could be a good candidate for CO₂ storage are introduced.

STORAGE MECHANISMS

Mechanisms based on geological factors

The efficiency of geological storage is defined as the amount of CO₂ stored per volume [9]. It depends on the physical and the geochemical trapping mechanisms. As it is shown in Figure 2, the extent of residual and solubility trapping of CO₂ are increased over time.

Carbon dioxide is trapped permanently when it becomes immobile, which is the most favorable types of storage. This would happen when the CO₂ saturation is low enough, which may be resulted by trapping under a suitable seal or by adsorbing on the rock or coal surface.

Physical Trapping

a. Stratigraphic and structural trapping

The primary means of geological CO₂ storage is its trapping below caprocks such as shale or salt beds. Traps which are made by changes in rock types are called stratigraphic. [10]

Structural traps are formed by rocks with fold or fractures. Faults can act both as a seal or path for fluid flow [10]. Both of these types of traps are suitable for CO₂ storage, however, the injection pressure should be calculated and considered to avoid fracturing during CO₂ injection [11].

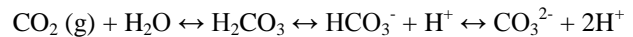
b. Residual trapping

Injected CO₂ displaces water and migrates upwards due to its lower density. Carbon dioxide moves as a separate phase until it traps as a residual phase. In saline formations, in which fluid migrates very slowly over long distances there is no need for any closed trap. Carbon dioxide can also dissolve in formation water and migrate within the formation [12]. Solubility trapping occurs when CO₂ dissolves in formation water, which eliminates the possibility of leakage through its buoyancy force.

Based on the modeling made by Holtz, at the end of the injection period, more than 60% of CO₂ is trapped by residual trapping and after about a thousand years all of the injected CO₂ is trapped by this mechanism [13].

Geochemical trapping

Carbon dioxide may be converted to carbonate minerals to form mineral trapping, the most slowly but the most stable form of geological storage mechanisms, which may take thousand years to occur [14]. This mechanism can be represented by the following chemical reactions:



The CO₂ solubility in the formation water increases by pressure but decreases by temperature and salinity.

Dissolution process produces an acid, which reacts with rock minerals (e.g. sodium, potassium) to form bicarbonate ions. Reaction time depends on some parameters such as pressure and temperature.

Perkins et al. studied the CO₂ storage in Weyburn oil field. They estimated that there would be no possibility for leakage over 5000 years, because the CO₂ would be either dissolved in water or converted into carbonate minerals. [15]

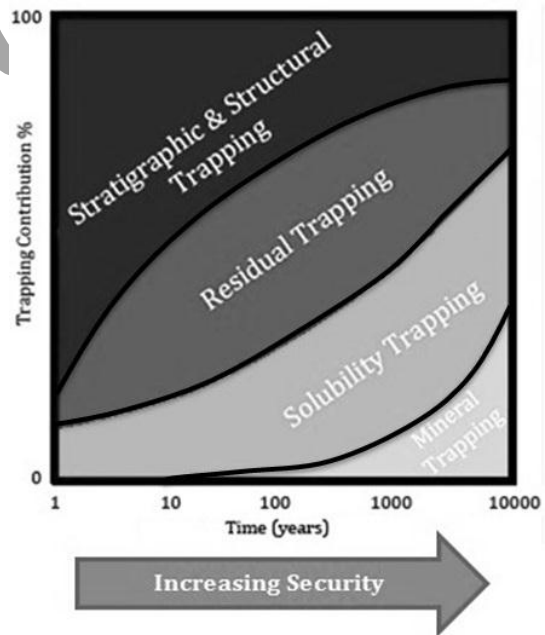


Figure 2

Storage securities depend on a combination of physical and geochemical trapping [1].

Mechanisms based on time scale

Some mechanisms start from the beginning of the injection, some others need much more time to take place. Different trapping mechanisms can be classified based on the time scale as follows:

Structural and stratigraphic trapping mechanisms, dominate over the first couple of years of injection, when the CO₂ moves as a separate phase.

During CO₂ displacement within the reservoir, which is saturated with oil or water, CO₂ stream becomes discontinuous and further improves the security of the CO₂ storage process [16, 17]. This mechanism is known as capillary or residual trapping.

Solubility trapping starts at the beginning of injection and becomes more important after long times. Water with dissolved CO₂ would be replaced by fresh water due to the higher density of CO₂-saturated water than the original density of fresh water. As a consequence of this free gravity convection more CO₂ can be dissolved in water. The dissolution depends on pressure, temperature, water salinity and the contact area between the water and the CO₂ phase. Dissolution trapping would enhance residual trapping mechanism.

Mineral trapping is the last but the most secure trapping mechanism, which has been estimated to become important after 1000 years. In this mechanism CO₂ becomes part of the solid matrix, thus there would be no concern in the context of CO₂ leakage.

RESOURCE-RESERVE PYRAMID

Carbon dioxide storage capacities should be estimated to evaluate available supplies and also to manage business processes [16, 18].

Resources are available volumes at a given time. There are two types of resources:

1. Discovered resources in which their location and characteristics are known.
2. Undiscovered resources that only are assumed to exist.

Reserves are capacities that are known to exist and recoverable.

The Techno-Economic Resource-Reserve pyramid for CO₂ storage capacity [16, 19] is shown in Figure 3. The size and position of each capacity varies in time (as the data and technology change.).

Theoretical storage capacity

It represents the maximum capacity for storage; in this case the whole bulk volume is accessible in stratigraphic and structural trapping, CO₂ dissolves or adsorbs at maximum saturation in solution or minerals, respectively. Theoretical storage capacity is not certainly accurate because of the physical, technical, regulatory and economic limits. [16]

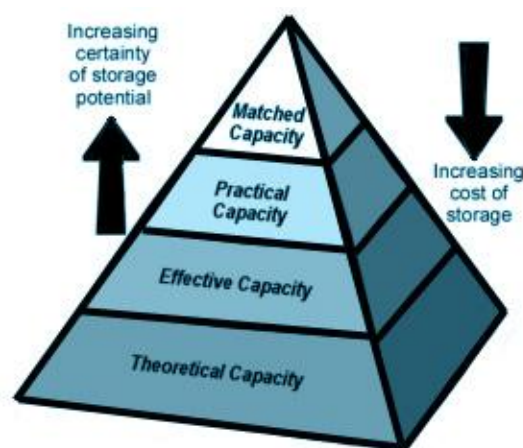


Figure 3

Techno-Economic Resource-Reserve pyramid of CO₂ geological storage capacity [16].

Effective (realistic) storage capacity

Effective capacity is obtained by considering the technical limits to the theoretical storage capacity such as that part of volume, which, cannot be physically accessed [16, 20].

Practical (viable) storage capacity

It is a part of the effective capacity attained with considering the technical (geological and engineering), regulatory, legal, infrastructure and economic limitations [16].

Matched storage capacity

Matched storage capacity is at the top of pyramid. It is obtained through complete matching of source with suitable storage sites [16].

SITE SELECTION CRITERIA

In order to have a successful storage the pertinent parameters, which could affect the storage process should be studied. These parameters include basin characteristics (e.g. acceptable porosity and permeability for good storage capacity and injectivity, respectively), resources (oil, gas, coal, etc.), industry developments, environmental issues, economy and etc. [21-24]. For example basins, which are behind the mountains, such as Zagros in Iran may be suitable for storage. However, those which are found in tectonically active areas such as areas in Pacific Ocean may not be suitable for storage because of the possibility of CO₂ leakage [24, 25].

Generally improper storage sites are those which are thin, faulted and fractured, without any suitable seal,

endured major diagenesis, with over-pressured reservoir.

Because storage is more effective when CO₂ is at the supercritical state (provides the potential for efficient utilization of underground storage space in the pores of sedimentary rocks), it is important to choose a caprock at a depth with desire temperature and pressure.

STORAGE SITES

Oil and gas fields

Abandoned oil and gas fields

One of the best site selections for CO₂ storage could be depleted hydrocarbon reservoirs, since they have reserved hydrocarbons for a long time. That is, they have suitable seal. Moreover, fluid properties have been studied and computer models have been utilized to simulate the whole reservoir. Some of the old infrastructures and wells can also be utilized for storage purposes [26]. However, it should be taken care of the possibility of leakage through abandoned wells [27] and also maximum endurable pressure to avoid fracturing the caprock [28, 29].

One of the most probable leakage pathways are injection and abandonment wells [30, 31]. Procedure of CO₂ storage from abandonment wells is different. Sealing and cement plugs, which are utilized should be CO₂ resistant. It is also better to remove the casing and liner to avoid possible corrosion which leads to leakage [32].

Figure 4 shows that in the case of abandonment wells, CO₂ can leak through the following pathways [30]:

- Between the inside of the casing and cement (a)
- Between the outside of the casing and cement (b)
- Within the cement plugs (c)
- Through casing (corrosion) (d)
- Through cement wall (e)
- Through cement and formation (f)

The leakage possibility through abandoned wells is a function of some parameters such as the number of wells contacted by CO₂, their depth and the abandonment method used (e.g. using corrosion-resistant cement plugs, removing all or part of the casing, etc.).

Enhanced oil recovery

By conventional recovery, 5-40 percent of the original oil in place (OOIP) is produced [33], 10-20 percent by secondary recovery (pressure maintenance methods) [34] and about 7 - 23 percent is produced

by enhanced oil recovery by using various methods such as CO₂ injection [35, 36].

Carbon dioxide can be injected as a continuous phase or with water as water alternating gas (WAG) method [37, 38]. The hydrocarbon and CO₂ phase behaviors, reservoir pressure and temperatures, CO₂ purity, oil compositions and gravity affect CO₂ injection process.

In order to use CO₂ as an enhanced oil recovery (EOR) agent, reservoir should have extra characters. For instance, deep (more than 600m), thin (less than 20m) and homogenous formations, high reservoir angle and low vertical permeability are desirable [38-41]. Heterogeneities may reduce the possibility of leakage by forcing CO₂ to spread laterally [34, 40 and 42].

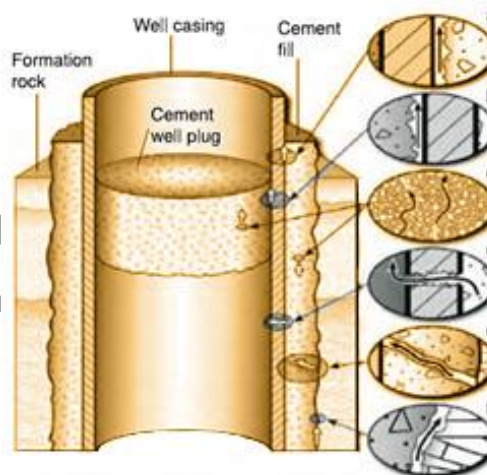


Figure 4

Possible leakage pathways in an abandoned well [30].

Enhanced gas recovery

About 95 percent of original gas in place (OGIP) can be produced by conventional recovery; CO₂ can be injected to maintain the pressure [43-45]. However, Clemens and Wit recommended that CO₂ injection in heterogeneous gas fields might have negative effects on the ultimate recovery [46].

Saline formations

Saline formations are deep sedimentary rocks saturated with formation water or brines. They have massive amounts of water that cannot be used for agriculture or human consumption.

Sleipner Project in the North Sea is the first industrial CO₂ storage project in saline formations, which started in October 1996. It is estimated that about 20Mt CO₂ would have been stored by the end

of project [47]. Based on experimental studies, CO_2 saturated brine becomes heavier and consequently the possibility of leakage reduces due to sinking in the aquifer [48].

Coal seams

Figure 5 shows that coals have more attraction to adsorb CO_2 compared to other gases such as methane and nitrogen [49]. In coal seams CO_2 can be injected for both storage and enhancing coal bed methane (ECBM) recovery. There are also some uncertainties in trapping mechanisms for temperatures and pressures above the critical point of CO_2 [50]. It has been shown that CO_2 has the potential to increase the methane production from 50% (conventional recovery) to 90% [51].

Carbon dioxide adsorbs about ten times more in mature coals such as anthracite, compared to the immature ones like lignite [49].

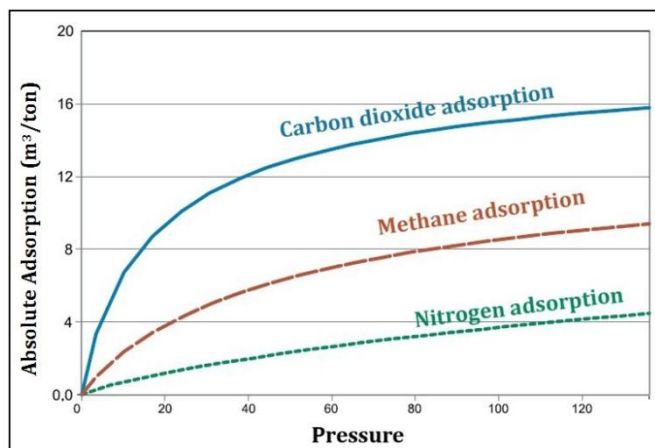


Figure 5

Pure gas adsorption on Tiffany coals (55°C) [49].

Injection of CO_2 into coal beds could decrease the permeability because of coal swelling [52], which may raise the injection pressure [50 and 53-55]. Zhang et al. suggested that injected CO_2 may react with coal [56]. Allison Project in the United States and Alberta Basin in Canada are a couple of successful cases of ECBM process [57].

Suitable fields for ECBM are those with high permeability, homogeneous structures, enough depth (down to 1500 m, greater depths have not yet been studied) and high methane saturation [58].

Reeves et al. suggested that high rank coal beds that are deep and have low permeability, which have not been developed previously for conventional coal bed methane (CBM) production, are favorable targets for ECBM [59].

In coal bed seams when CO_2 is in free phase the most possible pathways for leakage are faults and exploration wells during the injection [60, 61].

Basalts

Basalts have low porosity and permeability and any probable permeability is made by fractures, which increases the risk of leakage. Carbon dioxide, however, may react with silicates in the basalts. [62] Storage of CO_2 in basalts has many uncertainties that require further studies.

Oil or gas rich shale

Oil and gas shale may have the potential for CO_2 storage similar to coal beds, but this potential is currently unknown [1].

Salt caverns

Salt caverns could be a proper site for the CO_2 storage because of their high capacity, efficiency and injectivity. They have been used for natural gas storage for many years, but the storage of CO_2 in these structures is a different process. That is, natural gas is injected and produced regularly, but once CO_2 is injected it is not going to be produced, thus the storage site should be suitable for the large time scales.

Because of the high potential of release, a good sealing is very important in salt caverns to prevent leakage through the formation [63].

Abandoned mines

The rocks above the mines are fractured, which increases the potential of CO_2 leakage, however, abandoned coal mines may have a good potential for storage because of their capacity and the possibility of CO_2 adsorption onto the residual coal [64].

Ocean storage

Carbon dioxide can be transported with pipeline or ships to inject in the oceans or seas. There is no theoretical limit for ocean storage capacity, but injection of CO_2 in oceans results in the considerable change in ocean chemistry such as reduction of pH, which can harm marine organisms.

Kheshgi and Archer simulated the concentration of CO_2 in the atmosphere for different scenarios. In their study, 18,000 Gt CO_2 was injected to the atmosphere or ocean after 2050. The results of different scenarios are described below: [65-67]

Case 1: Carbon dioxide was totally released to the atmosphere, which lead to a peak in CO_2 concentration in the atmosphere.



Case 2: Carbon dioxide with the same ratio (i.e. half and half) was injected and released to ocean and atmosphere, respectively. It can be considered as the average between cases 1 and 4.

Case 3: 50% of Carbon dioxide was released to the atmosphere and the rest was used by other approaches; it has the same trend as case 1, however, with a half ratio.

Case 4: Carbon dioxide was totally injected to the ocean. As it can be seen in Figure 6, due to the equilibrium between the ocean and the atmosphere both curves in cases 1 and 4 converged to the same value. It shows that CO₂ injection into ocean (at depth 3000m) would have the same effect as releasing to the atmosphere (Case 1).

Case 5: Indicates no emissions, neither in the atmosphere nor in the ocean.

Carbon dioxide can also be injected at depths below 3000m, where CO₂ is denser than sea water to form CO₂ lakes on the sea floor.

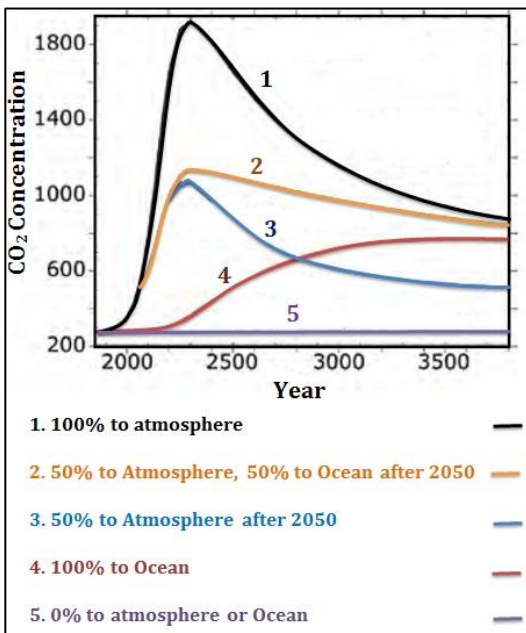


Figure 6
Different CO₂ release scenarios [65].

CO₂ EMISSION IN IRAN

Based on the statistical data, between 1967- 2007 in Iran, fossil fuel consumption and CO₂ emission increased about 617% and 610%, respectively [68]. Iran with 1.5% share of world CO₂ emission in 2004 was ranked as the 13th CO₂ emitter country [69]. Figure 7 shows that the power plants are the main CO₂ emitters in Iran with 28% of the total share, other main emitter sources are domestic use of energy, industry and transportation with 26%, 23%

and 16%, respectively [70]. The biggest Iranian industrial CO₂ emitters are listed in Table 1.

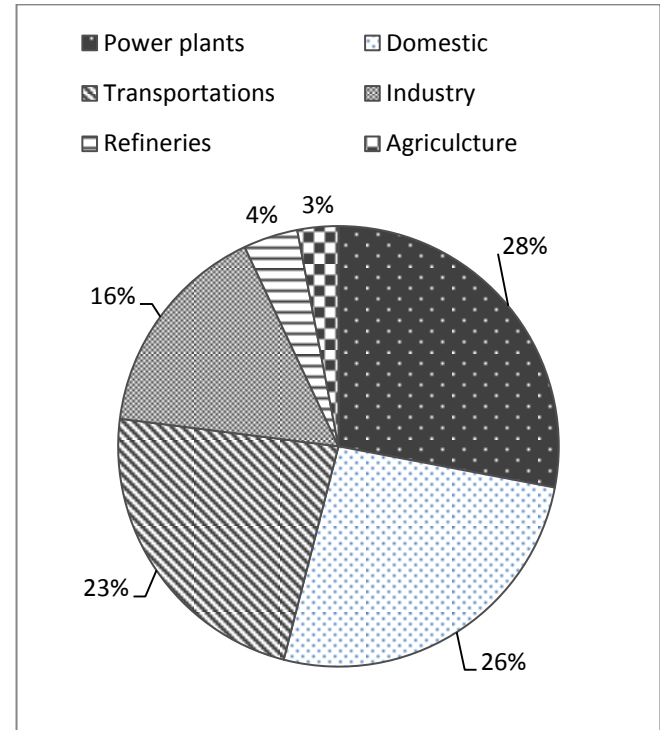


Figure 7
CO₂ emission in Iran [70].

Table 1
High CO₂ emission sources in Iran. [70]

Industry	Source	Location	CO ₂ purity	CO ₂ Emission (tone/y)
Petrochemical	Fars shimi	Asalooyeh	93.2	142000
	Maroon	Bandar mahshahr	6.2	110000
	Jam	Asalooyeh	6.2	900000
	Morvarid	Asalooyeh	93.2	178000
Gas Plants	Lavan	Asalooyeh	98	120000
	South pars	Asalooyeh	90	746000
Steel	Fajr-e-Jam	Booshehr	90	1071727
	Foolade khoozestan	Ahwaz	15	1500000
Cement	Fars	Shiraz	14.3	801993
	Darab	Shiraz	14.3	776562
	Karoon	Masjed soleyman	14.3	762452
	Khoozestan	Ramhormoz	14.3	699258
	Behbahan	Behbahan	14.3	547437
	Estahban	Shiraz	14.3	174044
	Dashtestan	Boshehr	14.3	432716
Other	Gharb	Kermanshah	14.3	257029
	Abadeh	Shiraz	14.3	165962

Based on the British Petroleum (BP) report at the end of 2010, Iran was the biggest natural gas producer in Asia and the third one in the world, with the 4.3% of total share. Iran has the second biggest proved reserve of natural gas (after Russia) with the

15.8% of the total reserve and is the third biggest consumer of natural gas (4.3% of total) [71]. Undoubtedly, production, treatment and consumption of such huge amount of gas emits huge amount of acid gases into the atmosphere. Table 2 illustrates that some gas processing plants in Iran with high sulfur concentration use sulfur reduction units (SRU) but yet there is no noticeable action for the reduction of CO₂ emission [66].

Table 2
Gas sweetening plants in Iran [70].

Refineries	Produced Reservoir	Acid gas Produced MMSCFD	Gas components		Recently position
			CO ₂ %	H ₂ S	
South pars (phase 1-5)	South pars	54	65-70	30-35	SRU
Fars jam	Nar & Kangan	64	97	3	Flare
Ilam	Tange bijar	35			SRU
Hashemi nejad	Mozdoran	160	65	35	SRU
Bid boland	Agha jari	3			Flare
Amak	Ahwaz marun	18	75	25	Flare
Farsi	Farsi	38	95	5	Flare
Sarkhon & Geshm	Sarkhon	67	98	2	Flare

Since, Iran has many suitable sites, which can be used for geological storage of CO₂, it is necessary to start reducing the CO₂ emission in Iran, by storing CO₂ underground.

STORAGE POTENTIAL IN IRAN

Iran has ten major lithotectonic areas which are Makran, the Lut Block, Eastern Iran, Kopet Dagh, the Alborz Mountains, the Central Iran Block, the Urumieh Dokhtar zone, the Sanandaj-Sirjan zone the Zagros fold belt and the Khuzestan plain [70-74]. The Zagros fold belt seems to be the best storage place because the South Pars which has the biggest gas reservoirs of country is located there.

Saeed et al., studied the Iranian geological structures potential for CO₂ storage, they considered three categories (feasibility, capacity and containment) for each formation. They concluded based on their studies, that Khalfani and Borkh geological structures have the high potential for geological storage. [70]

CONCLUSIONS AND SUMMARY

Based on this literature survey study, the following conclusions can be drawn:

- The most secure storage mechanism is mineral trapping in which CO₂ becomes part of rock, however, physical and solubility mechanisms are

the most important trapping mechanisms, because of increasing the security of storage at the shorter time.

- In physical trapping the caprock below which CO₂ is stored should be at a depth in which CO₂ is in its supercritical state.
- The feasibility of geological CO₂ storage in depleted oil and gas reservoirs and saline formations has been proved.
- Although depleted fields are suitable places for storage purposes, the possibility of leakage through abandonment wells should be taken care of.
- Further studies need to store CO₂ in coal beds; oil and gas shales, basalts, salt caverns and abandonment mines. Carbon dioxide can increase the methane production up to 90% and also has the potential to produce 7-23 percent of OOIP in enhancing oil recovery.
- Carbon dioxide emission in Iran is high and can significantly be reduced by using suitable formations for geological storage.
- Based on previous studies, Khalfani and Borkh are the best geological structures for CO₂ storage in Iran.

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