

TEHNOLOGIJE HVATANJA I SPREMANJA UGLJIKOVOG DIOKSIDA U ELEKTROENERGETSKOM SEKTORU – PREGLED RELEVANTNOG STANJA

CARBON DIOXIDE CAPTURE AND STORAGE TECHNOLOGIES IN THE ELECTRIC POWER SECTOR – OVERVIEW OF THE RELEVANT SITUATION

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U dolazećih pola stoljeća fosilna goriva će biti ekstenzivno korištena, a emisija CO₂ rasti, ukoliko ne bude provedena u djelo nova energetska politika. Postoje brojne opcije kojima se može reducirati emisija CO₂ iz energetskih sustava. One uključuju poboljšavanje energetske efikasnosti, prijelaz na obnovljivu i nuklearnu energiju. Međutim, politika temeljena na ovim opcijama će, u najboljem slučaju, samo djelomično riješiti problem. Tehnologije hvatanja, izdvajanja i spremanja ugljikovog dioksida sačinjavaju drugu obećavajući opciju koja može drastično reducirati ove emisije. Zbog tog razloga se hvatanje, izdvajanje, transport i skladištenje ugljikovog dioksida studiraju godinama. Brojni tehnički koncepti se predlažu; često spekulativne naravi – plod apstrakcije, daleko od iskustva i prakse. Mnogi od njih iziskuju vrlo velike istraživačke i razvojne napore prije komercijalizacije. Značajan napredak, napravljen u zadnjih desetak godina, omogućio je da se neka kompleksna tehnološka rješenja nalaze vrlo blizu komercijalne primjene. Ovaj članak omogućava kratak pregled relevantnog stanja tehnologija hvatanja, izdvajanja, transport i skladištenja ugljikovog dioksida koje će možda za dva desetljeća biti u širokoj primjeni u elektroenergetskom sektoru.

In the next half century, fossil fuels will be used extensively and the CO₂ emission will increase unless new energy policies are put through. There are numerous possibilities for the reduction of the CO₂ emission from the energy systems. These include the improvement of energetic efficiency and the switch to renewable and nuclear energy. However, the policy based on these options will, in the best case, solve the problem only partially. Carbon dioxide capture, isolation and storage technologies constitute the second, promising option which can drastically reduce these emissions. Because of that, carbon dioxide capture, isolation, transport and storage have been studied for years. Numerous concepts have been proposed, often of speculative nature- products of abstraction, far from experience and practice. Many of these require great research and developmental efforts before commercialization. Significant progress accomplished in the last ten years enabled some complex technological solutions to come close to commercial application. This article enables a short overview of the relevant situation in carbon dioxide capture, isolation, transport and storage, which could be widely used in the electric power sector two decades from now.

Ključne riječi: demonstracijska postrojenja; efikasnost; istraživanje; nadzor; neizvjesnost; planiranje; primjena; rizici; troškovi; značajke

Key words: application; costs; demonstration plants; efficiency; planning; properties; research; risks; supervision; uncertainty

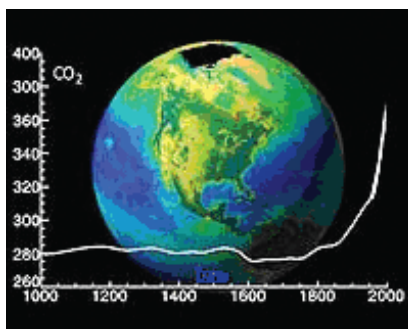


1 UVOD

Intenzivni razvitak industrije datira od sredine 19. stoljeća. Razvitak prati povećanje razine koncentracije ugljikovog dioksida u atmosferi sa **280 ppmi** (partes per milion mol) na skoro **370 ppmi** [1]. Nema točnog odgovora, kolika je granična koncentracija nakon koje će negativne i nepovratne klimatske promjene prouzročiti u konačnici propadanje ljudske civilizacije. Struka smatra da je ona bliže **450 ppmi** nego **750 ppmi**. Bez ikakvih mjera za smanjenje koncentracije ugljikovog dioksida u atmosferi bit će ga oko **900 ppmi** 2100. godine. Na slici 1 je prikazan porast koncentracije CO_2 u atmosferi od 1000. do 2000. godine.

1 INTRODUCTION

Intense industry development dates back to the mid-19th century. The development was accompanied by an increased concentration of carbon dioxide in the atmosphere from **280 ppmi** to almost **370 ppmi** [1] (ppmi – partes per million mol). There is no correct answer as to the amount of the cut-off concentration beyond which negative and irrecoverable climatic changes will finally cause the destruction of human civilization. The profession believes that it is closer to **450 ppmi** than to **750 ppmi**. Without any measures for the reduction of the carbon dioxide concentration in the atmosphere, in the year 2100, it will amount to about **900 ppmi**. Figure 1 shows the increase of the CO_2 concentration in the atmosphere from 1000 to 2000.



Slika 1 — Promjena koncentracija (ppmi) ugljikovog dioksida u atmosferi u zadnjih tisuću godina
Figure 1 — Change of carbon dioxide concentrations (ppmi) in the atmosphere in the last thousand years.

Stanje je alarmantno jer nije izglednija masovnija uporaba tehnologija za hvatanje, izdvajanje, transport i skladištenje (u nastavku HITS CO_2) u idućih 15 godina. Pretpostavlja se da će emisija ugljikovog dioksida porasti na **30 Gt CO_2** te da će se od **3 Gt CO_2** do optimističkih **76 Gt CO_2** [2] moći trajno zbrinuti u geološke naslage ispod zemlje. Sustav HITS CO_2 , proizvednog tijekom uporabe fosilnih goriva, može se izgraditi na postojećim tehnologijama. Sve aktivnosti su već pojedinačno implementirane u određenim aplikacijama na komercijalnoj razmjeri. Danas, niti jedan HITS CO_2 sustav u svijetu ne djeluje na komercijalnim postrojenjima za proizvodnju električne energije.

Proizvodnja električne energije ostvarena loženjem fosilnih goriva je odgovorna za više od **30 %** ukupne današnje emisije CO_2 . Uspoređujući druge opcije ublažavanja emisije CO_2 u elektroenergetskom sektoru, HITS CO_2 treba manja restrukturiranja sustava energetske dobave, pa čak i u samo nekoliko izvedenih projekata se može postići značajan utjecaj na emisije CO_2 na državnoj ili regionalnoj razini.

The situation is alarming because a more extensive use of capture, isolation, transport and storage technologies (hereinafter: CITS CO_2) in the next 15 years is not probable. The assumption is that carbon dioxide emission will increase to **30 Gt CO_2** and that from **3 Gt CO_2** up to the optimistic amount of **76 Gt CO_2** [2] could be permanently put into geological underground deposits. The CITS CO_2 system, produced during the use of fossil fuels, can be built on existing technologies. All the activities have already been separately implemented in certain applications at commercial levels. Today, none of the CITS CO_2 systems in the world are applied on commercial plants for the production of electricity.

Electricity production realized by the firing of fossil fuels is accountable for more than **30 %** of today's total CO_2 emission. By comparing other options for CO_2 emission amelioration in the electric power sector, the CITS CO_2 requires less restructuring of the energy supply system, and therefore in only a few executed projects a significant impact on CO_2 emission can be achieved at the national or regional level.

Važno je naglasiti da industrijski procesi generiraju oko 23 % emisije CO₂ u svijetu, a moguće je realizirati HITS CO₂ tijekom proizvodnje željeza, cementa, kemikalija i papira. U nekim slučajevima troškovi HITS-a mogu biti i niži nego u proizvodnji električne energije. Problem je što su jedini izvori emisije manji od elektroenergetskih, tako da je njihovo povezivanje glede transporta CO₂ složenije i skuplje.

U članku je dan pregled razvoja značajnih tehnoloških rješenja na kojima je zasnovan kompleksan sustav za hvatanje, izdvajanje, transport i skladištenja CO₂. Kvantificirane su njegove tehničke značajke, za koje tek treba razviti odgovarajući globalni sustav poslovanja. Međunarodna agencija za energiju (IEA) je pokrenula 1991. godine provedbu Programa razvoja i istraživanja stakleničkih plinova (u nastavku IEA GHG). IEA GHG je kroz međunarodnu suradnju, 26 zemalja članica i Europske (EU) komisije, inicirala razvoj tehnologija sposobnih za postizanje velikog smanjenja emisije stakleničkih plinova. IEA značajno organizacijski i financijski pomaže provedbu Programa, utječe na dinamiku napredovanja niza projekata i objektivno godišnje izvješćuje o njihovom napredovanju.

2 SVOJSTVA UGLJIKOVOG DIOKSIDA

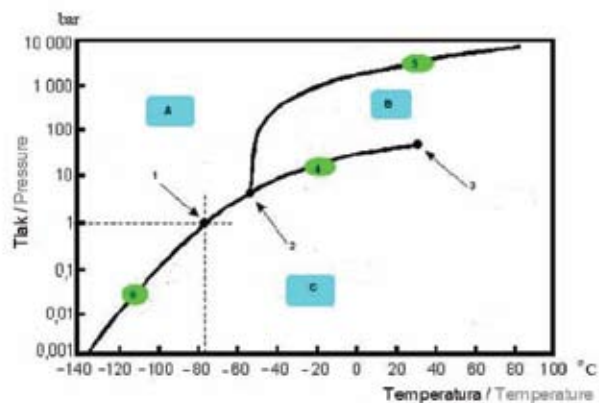
Pri normalnoj temperaturi i tlaku je ugljikov dioksid u plinovitom stanju. Fizičko stanje varira s temperaturom i tlakom, kako je prikazano na slici 2. Pri niskim temperaturama CO₂ je u krutom stanju, zagrijavanjem se, ako je tlak ispod 5,1 bar, iz krutog stanja izravno sublimira u plinovito stanje. Na međutemperaturama (između temperature trojne točke -56,5 °C, i temperature kritične točke od 31,1 °C), uz uklanjanje proizvedene topline CO₂ može prelaziti od pare u tekuće stanje komprimiranjem na odgovarajućem tlaku ukapljivanja. Pri temperaturama višim od 31,1 °C (ukoliko je tlak viši od tlaka u kritičnoj točki, 73,9 °C), za CO₂ se kaže da je u nadkritičnom stanju u kojem se ponaša kao plin; pod doista visokim tlakom gustoća plina može veoma varirati približavajući se ili čak biti veća od gustoće tekuće vode. Ovo je značajan aspekt ponašanja CO₂ i osobito je značajan za njegovo odlaganje. Toplina se oslobađa ili apsorbira pri svakoj promjeni faza/stanja preko granice kruto-plinovito i tekuće-plinovito. Međutim, fazne promjene iz nadkritičnog stanja u tekuće ili iz nadkritičnog stanja u plinovito ne zahtijevaju ili oslobađaju toplinu. Ovo svojstvo je korisno za projektiranje uređaja za komprimiranje. Značajnija fizička svojstva CO₂ su prikazana u tablici 1.

It is important to point out that industrial processes generate about 23 % of CO₂ emissions in the world, and it is possible to realize CITS CO₂ in the course of the production of iron, cement, chemicals and paper. In certain cases, the CITS costs can be even lower than those in electricity production. The problem is that unit emission sources are smaller than the electrical energy sources, therefore, their interconnection as regards CO₂ transport is more complex and more expensive.

The article depicts the overview of the development of significant technological solutions on which the complex system for the capture, isolation, transport and storage of CO₂ is based. Its technical properties are quantified and for these an adequate global business operation system still needs to be developed. In 1991, the International Energy Agency (IEA) launched the implementation of the Greenhouse Gas Research and Development Programme (hereinafter: IEA GHG). By virtue of international cooperation of 16 EU member states and the European Commission, the IEA GHG initiated the development of technologies capable of achieving significant reduction of greenhouse gas emissions. The IEA significantly supports the implementation of the Programme organizationally and financially, it impacts the dynamics of the progress of a number of projects and issues objective annual reports on their progress.

2 CARBON DIOXIDE FEATURES

At a normal temperature and pressure, carbon dioxide is in gaseous state. Its physical state varies depending on the temperature and the pressure, as shown in Figure 2. At low temperatures, CO₂ is in gaseous state, and, when heated, if the pressure is lower than 5,1 bar, from solid state it directly sublimates into gaseous state. At inter-temperatures (between the triple point temperature of -56,5 °C and the critical point temperature of 31,1 °C), with the removal of the generated heat, CO₂ can change from gaseous to liquid state by compression at the adequate liquification pressure. At temperatures higher than 31,1 °C (if the pressure is higher than the pressure at the critical point, 73,9 °C), CO₂ is said to be in supercritical state in which it behaves as gas; at a very high pressure, gas density may vary significantly and come close to or even higher than liquid water density. This is an important aspect of CO₂ behaviour and it is especially important for its disposal. Heat is released or absorbed at any change of phase/state over the solid-gaseous and liquid-gaseous boundary. However, phase changes from supercritical state to liquid or from supercritical state to gaseous do not require or release heat. This feature is useful for the design of compression devices. Key physical features of CO₂ are shown in



- 1 – Točka sublimacije / Sublimation point
 2 – Trojna točka / Triple point
 3 – Kritična točka / Critical point
 4 – Temperatura zasićenja / Saturation temperature
 5 – Temperatura taljenja / Melting temperature
 6 – Temperatura sublimacije / Sublimation temperature

A – Kruto stanje / Solid state
 B – Tekuće stanje / Liquid state
 C – Plinovito stanje / Gaseous state
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Slika 2 – Fazni dijagram za CO₂
 Figure 2 – Phase diagram for CO₂

Tablica 1 – Fizička svojstva ugljikovog dioksida
 Table 1 – Carbon dioxide physical properties

Svojstvo / Property	Vrijednost / Value
Molekularna težina / Molecular weight	44,01
Kritična temperatura / Critical temperature, °C	31,1
Kritični tlak / Critical pressure, bar	73,9
Kritična gustoća / Critical density, kg/m ³	467
Temperatura u trojnoj točki / Triple point temperature, °C	- 56,5
Tlak u trojnoj točki / Triple point pressure, bar	5,18
Točka ključanja (sublimacije) na / Boiling (sublimation) point at 1,013 bar, °C	- 78,5
Plinovita faza / Gaseous phase	
Specifična gustoća u točki ključanja / Specific density at the boiling point (1,013 bar), kg/m ³	2,814
Specifična gustoće STP / Specific density STP, kg/m ³	1,976
Specifični volumen STP / Specific volume STP, kg/m ³	0,506
Viskozitet (STP) / Viscosity (STP), μPa · s	13,72
Topivost u vodi (STP) / Solubility in water (STP), vol/vol	1,716
Entalpija (STP) / Enthalpy (STP), kJ/mol	21,34
Tekuće stanje / Liquid state	
Tlak pare / Vapour pressure (pri / at 20 °C), bar	58,5
Gustoća tekuće faze / Liquid phase density (-20 °C i / and 19,9 bar), kg/m ³	1032
Viskozitet (STP) / Viscosity (STP), μPa · s	99
Kruto stanje / Solid state	
Gustoća CO ₂ u točki zaleđivanja / CO ₂ density at freezing point, kg/m ³	1562
Latentna toplina isparavanja / Latent vaporization heat (1,013 bar u točki sublimacije / at sublimation point), kJ/kg	571,1

Napomena: STP standardna temperatura i tlak, jednaki 0 °C i 1,013 bar. Izvor: Air Liquid gas data table (Kirk-Otmer, Encyclopedia of Chemical Technology 1985)

Remark: STP standard temperature and pressure, equal to 0 °C and 1,013 bar. Source: Air Liquid gas data table (Kirk-Otmer, Encyclopedia of Chemical Technology 1985)

3 TEHNOLOGIJE HVATANJA I IZDVAJANJA CO₂

Tehnologije hvatanja i izdvajanja CO₂ (u nastavku HICO₂) se temelje na: apsorpciji (kemijska i fizička), adsorpciji, kriogenim postupcima i membrana. Trenutačno su u pogonu apsorpcioni reaktori dnevnog kapaciteta manjeg od 1 000 t CO₂. Klasični termoenergetski blok električne snage od 250 MW ložen kamenim ugljenom dnevno emitira oko 4 500 t CO₂, a kombi blok ložen prirodnim plinom jednake snage oko 2 150 t CO₂. To znači da bi se za veće proizvodne jedinice, postrojenje za HI moralo izgraditi od većeg broja manjih jedinica, to bi za posljedicu imalo povećana ulaganja, veliku vlastitu potrošnju i dvojbenu sigurnost pogona. Stručni krugovi očekuju da će bar jedna od tri glavne skupine tehnoloških postupaka, prikazane na slici 3, moći biti komercijalno primijenjena, u sljedećih deset do petnaest godina kod velikih proizvodnih jedinica u elektroenergetskom i industrijskom sektoru za hvatanje i izdvajanje CO₂ iz fosilnih goriva [3], [4] i [5]:

- hvatanje i izdvajanje ugljikovog dioksida nakon izgaranja (HICO₂-NI),
- hvatanje i izdvajanje ugljikovog dioksida prije izgaranja (HICO₂-PI),
- hvatanje i izdvajanje ugljikovog dioksida izgaranjem u struji kisika (HICO₂-Ox).

Mogućnost njihove primjene se temelji na komponentama provjerenima u komercijalnom pogonu kao što su rafinacija nafte, procesuiranje prirodnog plina i proizvodnja sintetičkih goriva. Trenutačno ne postoji u pogonu termoenergetsko pokazno postrojenje s potpunim HICO₂, u kojem bi se mogli provjeriti tehnički i komercijalni pokazatelji poslovanja.

Svi ostali tehnološki postupci za termo-elektroenergetska postrojenja su spekulativne naravi, često utemeljeni samo na laboratorijskim opitima ili pilot postrojenjima čije specifične rezultate rada je vrlo teško generalizirati.

Trenutačno se može izgraditi i staviti u funkciju HICO₂ za dekarbonizaciju fosilnih goriva u proizvodnji vodika (izdvajanje prije izgaranja) ili za hvatanje i izdvajanje CO₂ iz dimnih plinova nakon nekih industrijskih procesa (izdvajanje nakon izgaranja). Poboljšanja, u praksi dokazanih tehnologija manjih jediničnih snaga, uključuju razvoj novih kemijskih i fizičkih otapala za CO₂ s ciljem smanjenja energetskih potreba procesa izdvajanja. Za novije procese, istraživanja se usmjeravaju na bolje i jeftinije membrane za postupke povećanja koncentracije CO₂, efikasniju tehnologiju razdvajanja zraka (neke opcije uključuju izgaranje u čistom kisiku), jeftinije i efikasnije gorive ćelije (za pretvaranje kemijske

3 CO₂ CAPTURE AND ISOLATION TECHNOLOGIES

CO₂ capture and isolation technologies (hereinafter CICO₂) are based on: absorption (chemical and physical), adsorption, cryogenic procedures and membranes. At the moment, absorption reactors which are in operation are of daily capacity below 1000 t CO₂. The classic thermal energy block of 250 MW fired by hard coal emits about 4 500 t CO₂ daily, and the combined block fired by natural gas of equal power emits about 2 150 t CO₂. This means that for larger production units, the CI plant should be built from a larger number of smaller units which would result in significant investments, extensive own spending and uncertain safety of the plant. Expert circles expect that at least one of the three main groups of technological procedures, shown in Figure 3, could be commercially applied in the next ten to fifteen years in large production units in the electric power and industrial sector for the capturing and isolation of CO₂ from fossil fuels [3], [4] and [5]:

- capture and isolation of carbon dioxide after combustion (CICO₂-AC),
- capture and isolation of carbon dioxide before combustion (CICO₂-BC),
- capture and isolation of carbon dioxide by oxygen (CICO₂-Ox),

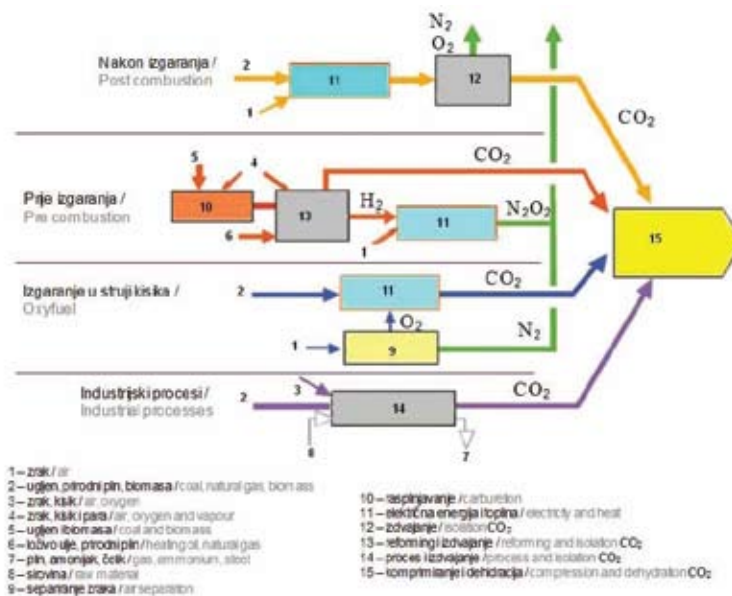
The possibility of their application is based on the components tested in commercial plants such as oil refinery, processing of natural gas and production of synthetic fuels. At the moment, no thermal energy demonstration plant with complete CICO₂, in which the technical and commercial business indicators could be tested, is in operation.

All other technological procedures for thermal-electric power plants are of speculative nature, often based only on laboratory tests or pilot plants the specific results of the work of which are difficult to be generalized.

Now, a CICO₂ for decarbonisation of fossil fuels in hydrogen production (isolation before combustion) or for the capture and isolation of CO₂ from flue gases after certain industrial processes (isolation after combustion) can be constructed and put into operation. Improvements of technologies of smaller unit powers proven in practice include the development of new chemical and physical solvents for CO₂ with the aim to reduce energy requirements of the isolation process. For newer processes, research is focused on better and cheaper membranes for the CO₂ concentration increase processes, more efficient air separation technology (some options include combustion in pure oxygen), cheaper and more efficient combustive

energije spremijene u vodik u metanu u električnu energiju), turbine na vodik, kemijske petlje itd. U tablici 2 prikazane su mogućnosti smanjenja emisije CO₂ iz nekih fosilnih goriva.

cells (for the transformation of chemical energy stored in hydrogen or methane into electricity), hydrogen-driven turbines, chemical loops, etc. Table 2 shows the possibilities of reduction of CO₂ emission from certain fossil fuels.



Slika 3 – Tri glavne opcije za hvatanje CO₂ iz termoelektrana
Figure 3 – Three main options for the capture of CO₂ from thermal power plants

Tablica 2 – Procjena tehnologija glede mogućnosti smanjenja emisije CO₂ [2]
Table 2 - Evaluation of technologies as regards the possibilities of reduction of CO₂ emission [2]

Procjena mogućnost tehnologija za 2020. godinu / Evaluation of technologies' possibilities for the year 2020	Ugljen / Coal	Loživo ulje / Heating oil	Prirodni plin / Natural gas
g CO ₂ /kWh (bez HITS/ without CITS)	900	660	330
g CO ₂ /kWh + HITS/CITS	108	-	54
Udio, %, uhvaćenog od emitiranog / Share, %, of captured out of the emitted	90	-	85
Dodatno gorivo za pogon HITS opreme, % od izvornog koncepta bez HITS / Additional fuel for the CITS equipment drive, % of original concept without CITS	20	-	10

Kod korištenja kamenog ugljena (tablica 3) prednost se daje tehnologiji HICO₂-PI, kod koje se izdvajanje obavlja u struji dimnih plinova s povećanom koncentracijom CO₂ budući da se rasplinjavanje obavlja u struji čistog kisika bez nazočnosti dušika. Nužno je naglasiti da još nije, nakon dugogodišnjih istraživanja, postignuta konkurentnost postrojenja za rasplinjavanje kamenog ugljena. Klasična tehnologija spaljivanja ugljene prašine je još uvijek bez konkurencije glede učinka, raspoloživosti, pouzdanosti i trajnosti opreme. Niti jedno postrojenje u svijetu ne rasplinjava na komercijalnoj osnovici kameni ugljen, već samo ostatke prerade nafte u rafinerijama. Izgaranje kisikom,

When using hard coal (Table 3), preference is given to the CICO₂-BC technology in which the isolation is performed in the flue gases current with an increased CO₂ concentration because the carburetion is performed in the pure oxygen current without the presence of nitrogen. It is important to point out that, in spite of years of research, competitiveness of the hard coal carburetion plants has not been achieved yet. Classic technology of coal dust combustion is still unparalleled as regards the effect, availability, reliability and durability of equipment. None of the world plants perform the carburetion on the hard coal commercial basis, but only on the basis of the waste from oil proce-

HICO₂-Ox, pokazuje dobre rezultate na jednom malom pokaznom postrojenju toplinske snage od 30 MW, ali na pitanja o životnom vijeku opreme kotlovsog postrojenja nema odgovora. Izgaranje u struji kisika, HICO₂-Ox, je po ocjeni struke u prednosti kod dogradnje na postojeća postrojenja budući da je potrebno izgraditi samo novo kotlovsko postrojenje; postojeće parno-turbinsko postrojenje ostaje u funkciji.

ssing in refineries. Oxyfuel, CICO₂-Ox, shows good results on one small demonstration plant with 30 MW (thermal), but it does not have answers as regards the life span of the boiler plant equipment. According to professional judgement, oxyfuel, CICO₂-Ox is in an advantageous position when it comes to upgrading of the existing plants because the only thing that is required is the construction of a new boiler plant; the existing steam-turbine plant remains in operation.

Tablica 3 - Usporedba efikasnosti i troškova hvatanja i izdvajanja CO₂ iz elektrana loženih ugljenom [5], [6] i [7]
Table 3 - Comparison of efficiency and isolation of CO₂ from the coal-fired power plants [5], [6] and [7]

Tip HICO ₂ tehnologije / Type of CICO ₂ technology	HICO ₂ -AC		HICO ₂ -BC		HICO ₂ -Ox + DESOx	
Izvor podataka / Information source	2003 IAE GHG		2003 IEA GHG		2002 CTH Lippendorf projekt / project	
Tip proizvodne jedinice / Production unit type	klasični / classic	+ HICO ₂	klasični / classic	+ HICO ₂	klasični (zrak) / classic (air)	Kisikom / oxygen + HICO ₂
Termoelektrana na ugljen / Coal-fired thermal power plant	Prašina / Dust	Prašina / Dust	Rasplinjavanje / Carburetion	Rasplinjavanje / Carburetion	Lignit prašina / Lignite dust	Lignit prašina / Lignite dust
Jedinična snaga / Unit power, MW _e	500	362	776	676	865	681
Neto efikasnost / Net efficiency, %	46	33	43	34	43	34
Emisija / Emission CO ₂ , kg/MWh _e	722	148	763	142	858	69
Uhvaćeno / Captured CO ₂ , kg/MWh _e	-	850	-	809	-	1085
Izbjegnuta emisija u zrak / Avoided emission into air, kg/MWh _e (*)	-	574	-	621	-	852
Specifično ulaganje / Specific investment, EUR/kW _e (**)	1020	1855	1370	1860	1270	1790
Trošak pogona i održavanja / Cost of operation and maintenance, EUR/MWh _e	7	13	12	16	3,9	3,9
Trošak izbjegnutog CO ₂ / Cost of avoided CO ₂ , EUR/t CO ₂	0	39,3	0	23,1	0	14,7

Napomena / Remark:

(*) Izbjegnuta emisija u zrak = (CO₂ emisija kg/MWh_e iz klasičnog tipa elektrane) - (CO₂ emisija kg/MWh_e klasični + HICO₂) / Avoided emission into air = (CO₂ emission kg/MWh_e from the classic power plant type) - (CO₂ emission kg/MWh_e classic + CICO₂)

(**) ulaganja bez troška kapitala i građevinskog zemljišta na zelenoj livadi / investment without capital costs and construction land on green meadows

- procjene specifičnih ulaganja su napravljene prije naglog skoka opreme koncem 2008. godine za 50 % do 70 % / assessments of specific investments have been made before the abrupt leap, at the end of 2008, of 50 % to 70 %

- komprimiranje ugljikovog dioksida / compression of carbon dioxide na / at 100 bar.

Hvatanje i izdvajanje su energetske vrlo intenzivni tehnološki procesi koji imaju za posljedicu značajan porast potrošnje ugljena i prirodnog plina za vlastitu potrošnju. Raspon prirasta vlastite potrošnje procesa se kreće od oko 39 % za današnje izvedbe do očekivanih 6 % za napredne izvedbe u budućnosti iza 2025. Energetska efikasnost proizvodnje električne energije je jedan od preduvjeta za korištenje HITS u energetskom sektoru. Naknadna dogradnja HITS-a na vrlo efikasne kombi blokove ložene prirodnim plinom bi možda mogla

Energy-wise, capture and isolation are very intensive technological processes the consequence of which is significant increase of consumption of coal and natural gas for own consumption. The scope of increment of own process consumption fluctuates from about 39 % for today's performance up to the expected 6 % for advanced performances in the future after 2025. Electricity production energetic efficiency is one of the preconditions for the use of the CITS in the energy sector. Subsequent upgrading of the CITS to very efficient combi-

biti opravdana opcija, ukoliko cijena prirodnog plina bude dovoljno niska.

Noviji tehnološki postupci, često špekulativne naravi, zasnovani na separatorima, izgaranju kisikom u kombinaciji s naprednim rješenjima za njegovu proizvodnju, kemijskoj petlji i ćelijama goriva, smatraju se obećavajućim za smanjivanje vlastite potrošnje procesa HICO₂. Kombiniranje biomasom loženih postrojenja za rasplinjavanje goriva s HITS-om može postati veoma prihvatljivo, čak i za mnogo manja postrojenja od ugljenom loženih postrojenja za rasplinjavanje i to zbog dvostruke koristi od CO₂ u usporedbi prema ugljenu s HITS-om. Takva kombinacija ima negativnu emisiju, jer se ugljik iz biomase temelji na CO₂ koji je uhvaćen iz atmosfere (i može ponovno biti vraćen ili izdvojen).

4 TEHNOLOGIJA TRANSPORTA IZDVOJENOG CO₂

CO₂ može biti transportiran cjevovodima, željezničkim cisternama i brodovima. U praksi, zbog velikog volumena, jedino su transport cjevovodima i brodovima troškovno prihvatljivi. Općenito se smatra da transportni troškovi, bez obzira na rastojanja i količine, trebaju biti manji dio ukupnih troškova HITS-a. Troškovi transporta CO₂ po jedinici težine su daleko niži, nego za prirodni plin ili vodik, jer je CO₂ u tekućem ili nadkritičnom stanju 10 do 100 puta veće gustoće. Zbog toga je, po jedinici težine, transport CO₂ troškovno mnogo sličniji transportu nafte nego prirodnog plina ili vodika. Inženjerska studija za termoelektranu Karsto u Norveškoj, na prirodni plin, ukazuje da transport cjevovodom predstavlja 40 % ukupnih ulaganja u HITS. Opisani slučaj je specifičan jer će se cjevovod velikih dimenzija polagati površinski zbog specifičnih geoloških uvjeta.

Transport cjevovodom je nepobitno dokazana tehnologija u dugogodišnjoj praksi i ne predstavlja poseban rizik, ukoliko se odabere odgovarajuća komercijalno provjerena oprema sukladna zakonskoj regulativi. Trenutačno je na globalnoj razini aktivno oko 3 100 km cjevovoda, godišnjeg kapaciteta oko 45 Mt CO₂ na tlaku 120 bar do 140 bar. Nije bilo incidenata velikog rizika po okoliš. Prikladno smješteni HITS projekti mogu značajno smanjiti potrebu za ekstenzivnim transportnim sustavima. Iznuđeni smještaj HITS projekata, poput postojećih lokacija termoelektrana, transportne sustave može povećavati stotinama kilometara, tada je nužno izgraditi magistralnu transportnu mrežu na koju bi bio priključen veći broj termoelektrana i spremnika CO₂ radi smanjenja troškova izgradnje i pogona.

nation blocks fired by natural gas could be a justified option if the natural gas price was low enough.

Recent technological procedure, often of speculative nature, based on separators, oxygen combustion in combination with advanced solutions for their production, the chemical loop and fuel cells, are considered promising for the reduction of own consumption of the CICO₂ process. Combining the biomass-fired carburetion plants with the CITS could become very acceptable, even for plants much smaller than the coal-fired carburetion plants and that because of the double benefit of CO₂ in comparison with the coal combined with the CITS. Such a combination has negative emission because the coal from the biomass is based on CO₂ captured from the atmosphere (which can be returned or isolated).

4 THE TECHNOLOGY FOR THE TRANSPORT OF THE ISOLATED CO₂

CO₂ can be transported by pipelines, railway tankers and ships. In practice, because of the extensive volume, only transport by pipelines and ships is acceptable as regards their costs. It is generally considered that transport costs, regardless of the distance and the quantities, have to be lower than the total CITS costs. The costs for the transport of CO₂ per weight unit are by far lower than for natural gas or hydrogen because CO₂ in liquid or supercritical state is of 10 or 100 times greater density. Thus, according to the weight unit, CO₂ transport is cost-wise much more similar to oil transport than to natural gas or hydrogen transport. Engineering study for the Karsto thermal power plant in Norway, fired by natural gas, shows that transport by pipelines makes 40 % of total investments into the CITS. The above case is specific because the large-size pipeline will be laid superficially due to specific geological conditions.

Transport by pipelines is a technology irrefutably proven through years of practice and does not represent a special risk if adequate, commercially tested, equipment, compliant with legal regulations, is chosen. At the moment, at the global level, about 3 100 km pipelines are active, and their annual capacity amounts to about 45 Mt CO₂ at the pressure of 120 bar to 140 bar. There were no incidents of high risk for the environment. Suitably positioned CITS projects could significantly reduce the need for extensive transport systems. The extorted location of CITS projects, such as the existing locations of thermal power plants, can expand the transport systems by hundreds of kilometres; therefore, it is necessary to build a main transport network onto which a significant number of thermal power plants and CO₂ reservoirs would be connected for the purpose of reducing construction and operation costs.

Materijali cjevovoda tijekom pogona mogu biti izloženi koroziji zbog prisustva SO_2 i vode (stvara se sumporna kiselina). Sumpor se pretvara u H_2S u anaerobnom okruženju (npr. CO_2 proces hvatanja u postrojenjima za rasplinjavanje fosilnih goriva), a i izgaranje u čistom kisiku ima za posljedicu stvaranje SO_2 . Ograničeno pročišćavanje CO_2 može stvarati dodatne troškove uklanjanja SO_2 . H_2S može bez problema biti injektiran zajedno s CO_2 , što je provjereno u Kanadi tijekom pogona u referentnom naftnom polju s 43 bušotine, organiziranom od Alberta Research Council i Alberta Energy Utilities Board [8].

Prijevoz izdvojenog CO_2 brodovima, gdje je to moguće, svakako treba razmatrati kao realnu opciju. Transport brodovima je nepobitno isplativa tehnologija za transport velikih količina, preko 1 000 t CO_2 . Trenutačno plove brodovi kapaciteta do 1 500 m³ CO_2 . Europska unija priprema projektnu dokumentaciju za brodove kapaciteta 20 000 m³. Brodski transport može postati veoma značajan, budući da se mnoga potencijalna podzemna spremišta ne nalaze u neposrednoj blizini izvora emisije CO_2 . Na primjer, većina budućih potencijalno značajnih spremnika su iscrpljena ležišta nafte na Srednjem Istoku, ili napuštena plinska polja u Rusiji i na Srednjem Istoku. Nasuprot njima, u industrijski razvijenim zemljama se nalaze glavni izvori emisije CO_2 . Sve dok se ne razvije međuregionalni transport (npr. Kina – Bliski Istok) iskorištavanje tih spremnika neće biti moguće. Kod naprednog korištenja metana istisnutog iz ležišta ugljena, transport CO_2 se općenito smatra tehnički jednostavnim budući da su specifična nalazišta ugljena rasprostranjenija bliže točkama emisije CO_2 .

Tekući CO_2 ima gustoću od 1,0 t/m³ do 1,5 t/m³ u usporedbi prema 0,454 t/m³ za ukapljeni prirodni plin (LNG). Spremnici za CO_2 se izrađuju od jeftinijih materijala jer se transport odvija na temperaturama od –50 °C u usporedbi prema –162 °C za LNG. Troškovi transporta brodom su približno jednaki transportu podmorskim cjevovodima na jednakom rastojanju od 500 km, dok je transport kopnenim cjevovodima duplo jeftiniji. Trenutačno bi interkontinentalni transport i troškovi spremanja CO_2 bili po vrlo grubim procjenama u rasponu od 25 USD/t CO_2 do 50 USD/t CO_2 za rastojanje oko 6 000 km. Procjena je temeljena na troškovima transporta LNG [8].

Globalna proizvodnja i brodski transport nafte iznose oko 3,5 Gt/god, globalna proizvodnja i transport ugljena iznose oko 3,8 Gt/god svjetska proizvodnja cementa je oko 1,6 Gt/god dok se oko 2,1 Gt/god žitarica preveze brodskim prostorom. Uz pretpostavku da je emisija CO_2 u svijetu oko 25 Gt/god; jednog dana možda ukupni brod-

During operation, pipeline materials can be exposed to corrosion due to the presence of SO_2 and water (sulphuric acid is generated). Sulphur turns into H_2S in an anaerobic environment (e.g. the CO_2 capture process in fossil fuels carburation plants), and the combustion in pure oxygen also results in the generation of SO_2 . Limited refinement of CO_2 can create additional costs of removal of SO_2 . H_2S can easily be injected together with CO_2 , which has been verified in Canada during operation in the relevant oil field with 43 boreholes, organized by Alberta Research Council and Alberta Energy Utilities Board [8].

The transport of the isolated CO_2 by ships, where possible, should absolutely be considered as a realistic option. Transport by ships is irrefutably a cost-effective technology for the transport of quantities over 1 000 t CO_2 . At the moment, ships with capacities of 1 500 m³ CO_2 are sailing. The European Union is preparing project documentation for ships with capacities of 20 000 m³. Ship transport could become very important because many potential underground reservoirs are not located in the direct vicinity of the CO_2 emission sources. For example, most of the reservoirs which could become important in the future are the exhausted oil deposits in the Middle East or the abandoned gas fields in Russia and the Middle East. As opposed to these, the main sources of CO_2 emissions are located in the industrially developed countries. Until interregional transport is developed (e.g. China - the Middle East) the exploitation of those reservoirs will not be possible. In advanced use of methane extracted from coal deposits, CO_2 transport is generally considered to be technically simple because the specific coal sites are more densely spread closer to the points of CO_2 emission.

Liquid CO_2 has a density of 1,0 t/m³ up to 1,5 t/m³ in comparison with 0,454 t/m³ for liquefied natural gas (LNG). CO_2 reservoirs are made of cheap materials because the transport takes place at temperatures of –50 °C in comparison with –162 °C for the LNG. Costs of transport by ship are about the same as those of transport by underwater pipelines taking the same distance of 500 km, while transport by continental pipelines is half as cheap. At the moment, intercontinental transport and costs of CO_2 storage would, as a very rough estimate, be in the scope from 25 USD/t CO_2 to 50 USD/t CO_2 for the distance of 6 000 km. The estimate is based on transportation costs for the LNG [8].

Global production and oil transport by ship amount to about 3,5 Gt/year of global production and transport of coal amount to about 3,8 Gt/year, global cement production is about 1,6 Gt/year while about 2,1 Gt/year of cereals are transported by ship. Under the assumption that the CO_2 emission in the world is about 25 Gt/year, one day, the total ship transport of CO_2 may come to the same level as the transport of all specified goods taken together! Because of

ski prijevoz CO₂ može biti istog reda veličine kao i transport svih specificiranih roba zajedno! Zbog toga izazovi koji stoje pred razvojem sustava za transport CO₂ nikako ne smiju biti podcijenjeni. Neki stručni krugovi smatraju organiziranje globalnog transporta upitnim u bliskoj budućnosti te polažu nade u razvoj spekulativne tehnologije uklanjanja ugljikovog dioksida iz zraka!

5 TEHNOLOGIJA SPREMANJA CO₂

Generalno, jedina realna opcija u idućem kratko-ročnom i srednjoročnom vremenskom periodu planiranja je podzemno skladištenje CO₂ u dubokim ležištima nafte, plina, ugljena i naslagama propusnih stijena koja sadrže vodu visokog saliniteta (u nastavku slani vodonosnik).

U drugi plan se stavlja mogućnost spremanje u oceane i nadzemno skladištenje i to zbog rizika po okoliš i problema koji mogu pratiti spremanje i nadzor spremljenog CO₂.

Teoretski potencijal i kapacitet spremanja CO₂ u duboke slane vodonosnike se procjenjuje na 1 000 Gt do 10 000 Gt, što omogućava spremanje decenijama i stotinama godina. Naslage slanih vodonosnika, kao potencijalnih spremnika, su daleko ravnomjernije raspoređene od ležišta nafte i prirodnog plina. Trenutačno vrlo uspješno radi odlaganje CO₂ u slani vodonosnik Sleipner (Norveška) [9] kapaciteta 1 000 kt/god. Usporedbe radi, proizvodna postrojenja Hrvatske elektroprivrede d.d. imaju godišnju emisiju oko 6 000 kt CO₂.

Duboka nalazišta plina i nafte mogu pohranjivati decenijama emisiju CO₂ uz prihvatljiv stupanj rizika. Injektiranje CO₂ radi unaprjeđenja iskorištenja ležišta fosilnih goriva može postati, rana i ključna, povoljna prilika za spremanje, i to posebno onda, kada se mogu ostvariti prihodi koji pokrivaju sve ili dio troškova HITS. Realizirano je nekoliko projekata od kojih je najveći lociran u Weyburnu (USA/Kanada) kapaciteta 2 000 kt/god s ciljem povećanja iscrpka nafte i Snøhvit (Norveška) 700 kt/god u slani vodonosnik. Projekti su pokazali pogonsku sposobnost spremanja CO₂ u podzemna skladišta. Svi navedeni projekti su namijenjeni za povećanje iscrpka nafte injektiranjem CO₂ ili kiselih plinova u bušotine. Potencijal ovakvih projekata nije do sada dovoljno distribuiran.

Trenutačno se istraživanje i razvoj tehnološkog postupka skladištenja fokusira na sljedeće opcije:

- povećanje iscrpka nafte utiskivanjem CO₂ u ležište, (u nastavku EOR)

that, the challenges which are set before the CO₂ transport system should not be underestimated no matter what. Some professional circles believe that the organization of the global transport in the near future is questionable and they have expectations as regards the development of speculative technology for the removal of carbon dioxide from the air!

5 CO₂ STORAGE TECHNOLOGY

Generally, the only real option in the following short-term and middle-term planning period is underground storage of the CO₂ in deep oil, gas and coal deposits and layers of porous rocks which contain high-salinity water (hereinafter: saline aquifer).

The position of second importance is given to the possibility of storage in oceans and surface storage and that without risk for the environment and the problems which could accompany the storage and supervision of the stored CO₂.

Theoretically, the potential and capacity of CO₂ storage in deep saline aquifers is estimated at 1 000 Gt up to 10 000 Gt which enables storage for decades and hundreds of years. Saline aquifers layers, as potential reservoirs, are far more equally spread than oil and natural gas deposits. At the moment, the storage of CO₂ into the Sleipner saline aquifer (Norway) [9] with the capacity of 1 000 kt/year is operating very successfully. For the purpose of comparison, the plants of Hrvatska elektroprivreda d.d. have annual emissions of about 6 000 kt CO₂.

Deep gas and oil sites can store CO₂ emissions for decades with an acceptable risk level. CO₂ injections for the purpose of improvement of employment of fossil fuel layers can become an early favourable chance for storage with key importance, especially when income can be realized which covers all or a part of the CITS costs. Several projects have been realized – the greatest of these is located in Weyburn (USA/Canada) and has a capacity of 2 000 kt/year – its purpose is enhanced oil recovery; and Snøhvit (Norway) has a capacity of 700 kt/year – into the saline aquifer. The projects have shown the plant's capability of storing CO₂ in underground reservoirs. All the above projects are intended for enhanced oil recovery by injection of CO₂ or acid gases into the boreholes. The potential of these projects has not been distributed enough so far.

At the moment, research and development of the technological process of storage focuses on the following options:

- enhanced oil recovery by CO₂ injection into the

- povećanje iscrpka prirodnog plina utiskivanjem CO₂ u ležište, (u nastavku EGR),
- povećanje iscrpka metana utiskivanjem CO₂ u ležišta ugljena, (u nastavku ECBM),
- spremanje u iscrpljena ležišta nafte ili prirodnog plina,
- spremanje u duboke slane vodonosnike (u nastavku SA),
- ostale opcije skladištenja.

U većem broju objavljenih studija se navodi da će troškovi skladištenja biti sekundarne važnosti u usporedbi s troškovima hvatanja i transporta. Tvrdnja je jedino točna ukoliko je trošak kompresije uključen u troškove hvatanja i transporta. Troškove je vrlo teško uprosječiti budući da osciliraju ovisno od slučaja do slučaja 5 (čak i 10) puta. Radi jednostavnije analize je pretpostavljena vrijednost tlaka skladišta od 100 bar. Tlak utiskivanja i rastojanje na koje se transportira određuju polazni tlak CO₂. Tlak utiskivanja je ovisan o dubini injektiranja i o tlačnom profilu u podzemlju. Minimalna dubina skladištenja je oko 800 m (na toj dubini je CO₂ u superkritičnom stanju). U superkritičnom stanju ne postoji vidljivi prijelaz iz plinovitog u tekuće stanje pri porastu tlaka. Gustoća CO₂ pri 100 °C i 200 bar je 0,5 t/m³ a pri 500 bar 0,8 t/m³. Lokalni tlak i temperatura određuju gustoću CO₂ i ona se obično kreće u rasponu od 0,61 t/m³ do 0,72 t/m³.

Većina potencijalnih spremnika je locirana na dubinama 2 km do 4 km ispod površine. Za spremnike na dubinama od 800 km, može biti dovoljan tlak utiskivanja od 100 bar. Međutim spremanje u iscrpljena ležišta plinskih polja će zahtijevati površinski tlak pred utiskivanjem od 200 bar do 300 bar, tablica 4. Sastavni dio tehnološkog postupka je i recirkuliranje CO₂, na čega se troši veoma značajna energija. Na primjer, u praksi kod povećanja iscrpka nafte utiskivanjem CO₂ u ležište, u stalnoj recirkulaciji se nalazi od 16 % do 40 % mase CO₂ koja se utiskuje (20 % do 67 % se obično u konačnici trajno zadrži u sloju!).

Kod povećanja iscrpka prirodnog plina utiskivanjem CO₂ u ležište, količina zadržanog i uskladištenog CO₂ u sloju, kojom se postiže željeni učinak, iznosi skromnih 14 %! Recirkulirana količina CO₂, kod opcije povećanja iscrpka metana utiskivanjem u ležišta ugljena, može biti vrlo velika ukoliko CO₂ kroz pukotine stijena obilazi ležište ugljena/metana ili ako samo ležište već sadrži veću količinu prirodnog CO₂. Prosječno se, u opciji utiskivanja u ležište ugljen/metan obično zadržava oko 20 %.

- deposit, (hereinafter EOR)
- enhanced natural gas recovery by CO₂ injection into the deposit, (hereinafter EGR)
- enhanced coal bed methane extraction by injection of CO₂ into coal beds, (hereinafter ECBM)
- storage in depleted oil or natural gas deposits,
- storage in deep saline aquifers (hereinafter: SA),
- other storage options.

A large number of published studies state that storage costs will be of secondary importance in comparison with capture and transportation costs. The claim is accurate only if the compression cost is included in capture and transportation costs. It is very difficult to determine the average of the costs because they oscillate, depending on the case, by 5 (even up to 10) times. For the purpose of a simpler analysis, the value of storage pressure is assumed to be 100 bar. The injection pressure and the distance of the transportation are the determinants of the initial CO₂ pressure. The injection pressure depends on the injection depth and the underground pressure profile. The minimum storage depth is about 800 m (at that depth, CO₂ is in supercritical state). At increase of pressure in supercritical state there is no evident transition from gaseous to liquid state. CO₂ density at 100 °C and 200 bar is 0,5 t/m³ and at 500 bar it is 0,8 t/m³. Local pressure and temperature determine CO₂ density and it usually fluctuates in the scope between 0,61 t/m³ up to 0,72 t/m³.

Most potential reservoirs are located at the depths of 2 km to 4 km beneath the surface. For the reservoirs at the depths of 800 km, injection pressure of 100 bar could suffice. However, storage in depleted gas fields will require a surface pressure prior to injection of 200 bar up to 300 bar, Table 4. An integral part of the technological process is also the recycling of CO₂ which consumes a significant amount of energy. For example, in practice, at enhanced oil recovery by injection of CO₂ into the deposit, there is about 16 % up to 40 % of CO₂ mass which is in constant recirculation and which is injected (20 % up to 67 % usually ends up in the layer permanently!).

At enhanced natural gas recovery by injection of CO₂ into the deposit, the amount of CO₂ retained and stored in the layer which enables the achievement of the desired effect, amount to a mere 14 %! The quantity of CO₂ in recirculation, at the enhanced coal bed methane extraction by injection into coal beds, may be very high if the CO₂ roams the coal/methane bed through rock fractures or if the bed itself already contains a large quantity of natural CO₂. At the bed injection option, coal/methane usually lingers at about 20 %.

Tablica 4 – Potrebna energija tlačenja CO₂ za injektiranje ovisno o vrsti spremnika i dubini [9]
 Table 4 - CO₂ pressing energy necessary for the injection depending on the type of reservoir and depth [9]

	Tlak od 100 bar na 800 m dubine / Pressure of 100 bar at the depth of 800 m, GJ/t CO ₂	Tlak od 200 bar na 1 600 m dubine / Pressure of 200 bar at the depth of 1 600 m, GJ/t CO ₂
Povećanje iscrpka nafte utiskivanjem CO ₂ / Enhanced oil recovery by CO ₂ injection	0,34	0,50
Povećanje iscrpka prirodnog plina utiskivanjem CO ₂ / Enhanced natural gas recovery by CO ₂ injection	0,25	0,40
Povećanje iscrpka metana utiskivanjem CO ₂ / Enhanced coal bed methane extraction by injection of CO ₂	0,25	0,40
Spremanje CO ₂ u duboke vodonosnike / Storage of CO ₂ into deep aquifers	0,22	0,38

5.1 Tehnološki postupci EOR i EGR

Povećanje iscrpka nafte utiskivanjem CO₂ u ležišta donosi najveće prihode u usporedbi s ostalim opcijama. U nekim posebnim slučajevima se spremanjem može jedno vrijeme ostvariti i čista dobit (diktirano potražnjom i cijenom barela nafte). Presudne su geološke formacije i lokacije ležišta u odnosu na izvor CO₂.

U pogonu je 2004. godine bilo 105 skladišta tipa EOR, od kojih se 85 nalazi u SAD i 8 u Kanadi. Veći broj projekata je u različitim stupnjima razvoja. Primarni i sekundarni načini iskorištavanja naftnih ležišta općenito imaju za posljedicu iscrpak između 40 % i 50 %. To ovisi od: kompleksnosti i uvjeta u ležištu, strategije iskorištavanja ležišta i ekonomskih kriterija. Dobivanje nafte tercijarnim metodama ili metodama povećanja iscrpka (EOR) ključni je proces nadomještanja ili povećanja rezervi koje se mogu koristiti na ekonomičan način, i to bez primjene konvencionalnih metoda. Utiskivanje raznih plinova se danas smatra drugom (prva je voda) po djelotvornosti metodom povećanja iscrpka nafte. Utiskivanje vode ili plinova u iscrpljena naftna polja povećava tlak u ležištu koji omogućava istiskivanje nafte iz šupljina stijena i strujanje prema proizvodnim bušotinama.

U SAD se tijekom 2003. godine proizvodilo oko 200 000 bbl nafte po danu utiskivanjem CO₂ u naftna ležišta. Ovaj postupak je zastupljen s udjelom od oko 31 % u ukupnoj proizvodnji nafte tercijarnim mjerama povećanja iscrpka. Preostalih 69 % čini utiskivanje dušika, dimnih plinova, ugljikovodika, vodene pare i polimera. Količine CO₂ utisnute radi povećanja iscrpka nafte iznose oko 32 000 kt/god CO₂ iz prirodnih izvora i oko 11 000 kt iz industrijskih procesa. Izvan SAD postoji nekoliko projekata u pogonu. EOR utiskivanje CO₂ radi povećanja iscrpka nafte se primjenjuje više od tri desetljeća i smatra se provjerenom tehnologijom. Međutim, ova tehnologija je razvijena

5.1 EOR and EGR technological procedures

Enhanced oil recovery by injection of CO₂ into the deposits yields the highest income in comparison with the other options. In certain special cases, the storage may, for a certain time, yield pure profit (dictated by demand and oil barrel price) as well. Geological formations and deposit locations as regards the CO₂ source are decisive.

In 2004, 105 storages of EOR type were in operation; 85 of these were located in the USA and Canada. A significant number of projects is in different developmental stages. Primary and secondary methods of oil deposit exploitation generally result in the extraction of between 40 % and 50 %. That depends on: deposit complexity and state, deposit exploitation strategies and economic criteria. Obtainment of oil by tertiary methods or enhanced oil recovery methods (EOR) is the key process for the substitution or increase of reserves which may be used in an economical manner and that without the application of conventional methods. Today, the injection of different gases is considered to be the second most effective method of enhanced oil recovery (the first being the injection of water). The injection of water or gases into depleted oil fields increases the deposit pressure which enables the oil to be extracted from the rocks' cavities and the circulation towards production boreholes.

During 2003, in the USA, about 200 000 bbl of oil were produced daily by injection of CO₂ into oil deposits. This procedure participates with about 31 % in the total oil production by virtue of tertiary enhanced recovery methods. The remaining 69 % includes the injection of nitrogen, flue gases, hydrocarbon, water vapour and polymers. Quantities of CO₂ injected for the purpose of enhanced oil recovery amount to about 32 000 kt/year CO₂ from natural sources and to about 11 000 kt from industrial processes. There are several operating projects outside the USA. EOR CO₂ injection for the purpose of enhanced oil recovery has been implemented for

s ciljem povećanja iscrpka nafte, a ne za trajno spremanje CO₂. Povećanje iscrpka nafte tercijarnim mjerama u prosjeku obično povećava ukupno iskorištenje naftnih polja do 50 %. EOR se ne može obično primijeniti na sva naftna polja. Dubina ležišta nafte obično mora biti veća od 600 m. Sirova nafta treba biti gustoće najviše 910 kg/m³, što čini ovu metodu nepodobnom za teške nafte, uljni pijesak ili ležišta s plinskom kapom. Utiskivanje CO₂ je ograničeno na naftna polja kod kojih je završena proizvodnja primarnim mjerama (tlak ležišta) i sekundarnim mjerama (pumpanje i utiskivanje vode). U slučaju velikih plinskih kapa efikasnost utiskivanja CO₂ je ograničena. Značajan dio utisnutog CO₂ se vraća s naftom i vodom na površinu; tada se CO₂ mora izdvojiti i ponovno utiskivati. Po zatvaranju naftnih polja angažirani CO₂ je trajno spremljen. Do temperatura ležišta od 120 °C, CO₂ se miješa s naftom, dok na višim temperaturama CO₂ nadomješta naftu. Povoljnije je miješanje CO₂ s naftom jer rezultira relativno većim iscrpkom. Miješanje CO₂ i nafte omogućava da se na tonu nafte utisne 2,4 t CO₂ do 3 t CO₂. Procjene potencijala spremanja u bušotine naftnih polja osciliraju i ovise o kriterijima selekcije (troškovi, geološka struktura, koncentracija polja). Nove utisne bušotine za EOR predstavljaju glavni dio ulaganja.

Za EOR treba postojati potencijal od minimalno 5 milijuna barela nafte i više od 10 bušotina. Tada bi ukupni pr fte oko 110 USD/t (15 USD/bbl), uz pretpostavljenu količinu utiskivanja od 2,5 t CO₂ po toni sirove nafte, dobit je oko 25 USD/t CO₂ za gratis količinu CO₂. Pretpostavljena dobit je proračunata za izvrsnu specifičnu utisnutu količinu, što kod većine ležišta nafte nije moguće postići, tako da je i dobit znatno manja.

U većini polja je nužno bušiti nove utisne bušotine, budući da su stare eksploatacijski nepouzdanе; zapažena su izbijanja CO₂ kroz zabrtvljene bušotine. Tehno-ekonomske analize opravdanosti mogu, zbog velikog broja nepoznanica podcijeniti potencijal tehnologije EOR; što je slučaj s utiskivanjem u polja Sjevernog mora kod kojih je iscrpak udvostručen.

EGR je teoretska metoda podizanja tlaka u iscrpljenim (oko 85 %) plinskim ležištima. Podobna iscrpljena ležišta metana imaju tlak od 20 bar do 50 bar. Bez obzira na stanje u kojem se nalazi, CO₂ (plinovito, tekuće ili superkrično) je značajno gušći od CH₄ pri svim relevantnim tlakovima i temperaturama i ima tendenciju strujanja na niže pri utiskivanju u bušotinu, što ima za posljedicu istiskivanje prirodnog metana i podizanje tlaka u ležištu. Utiskivanje CO₂ do 2007. godine nije korišteno u komercijalne svrhe. Postoje dvojbe oko opravdanosti primjene ove teoretske metode. Sve ovisi o vremenu potrebom da CO₂

more than three decades and is considered tested technology. However, this technology has been developed with the aim to increase oil recovery and not for permanent storage of CO₂. Enhanced oil recovery by tertiary measures usually increases the total exploitation of oil fields by up to 50 % in the average. The EOR usually cannot be applied to all oil fields. Oil deposit depth usually has to be over 600 m. Crude oil density has to be at the most, and this makes this method ineligible for heavy oils, oil sands or gas-cap deposits. CO₂ injection is limited to oil fields in which the production by primary methods (deposit pressure) and secondary methods (pumping and water injection) is completed. In case of large gas caps, the efficiency of CO₂ injection is limited. A significant share of the injected CO₂ comes back with oil and water onto the surface; CO₂ must then be separated and re-injected. After the sealing of the oil fields, the employed CO₂ is stored permanently. Up to the deposit temperatures of 120 °C, CO₂ is mixed with oil, while at higher temperatures, CO₂ substitutes oil. Mixing with CO₂ is more favourable because it yields relatively higher extraction ratios. Mixing CO₂ and oil provides for the injection of 2,4 t CO₂ up to 3 t CO₂ per ton of oil. Estimates of the potential of the storage in oil field boreholes vary and depend on the selection criteria (costs, geological structure, field concentration). New injection boreholes for the EOR constitute the major part of the investment.

The EOR requires the potential of at least 5 million oil barrels and more than 10 boreholes. Total production costs would then amount to (without the CO₂ cost) about 50 USD/t (7 USD/bbl). If at the top of the borehole the oil price is about 110 USD/t (15 USD/bbl) with the presumed amount of injection of 2,5 t CO₂ per ton of crude oil, the profit is about 25 USD/t CO₂ for a gratis amount of CO₂. The predicted profit is calculated for an excellent specific injected quantity and this cannot be achieved in most oil deposits and therefore the profit is lower as well.

In most of the fields, new injection boreholes need to be drilled because the old ones are unreliable for exploitation; CO₂ bursts through sealed boreholes have been recorded. Technological-economical justifiability analyses could, because of the large number of unknown terms, underestimate the potential of the EOR technology which is the case with the injections into the Northern Sea fields which yielded double extraction ratios.

EGR is the theoretical method of pressure increase in depleted (about 85 %) gas deposits. Eligible depleted methane beds have pressures of 20 bar up to 50 bar. Regardless of its state (gaseous, liquid or supercritical), CO₂ is significantly denser than CH₄ at all relevant pressures and temperatures and has the tendency of downward flow at injection into the borehole, the consequence of which is the extrac-

dopre do plinskog ležišta. Procjenjuje se da kapacitet spremanja CO₂ u plinska ležišta ima veći potencijal od mogućnosti spremanja u ležišta nafte. Tehno-ekonomskim analizama opravdanosti većeg broja projekata su utvrđeni značajno manji prihodi (npr. oko 1,8 GJ prirodnog plina se dobije utiskivanjem jedne tone CO₂) nego kod utiskivanje u ležišta nafte.

5.2 Spremanje u iscrpljena ležišta nafte ili prirodnog plina

Operacija spremanja je vrlo jednostavna budući da jedino treba izgraditi utisne bušotine (ovisno o geologiji polja i brzini utiskivanja). Veći dio postojeće infrastrukture se može iskoristiti, što znatno smanjuje ulaganja. U budućnosti će potencijal spremanja rasti jer će biti sve veći broj iscrpljenih ležišta nafte i plina i to naročito na Bliskom istoku i u zemljama bivšeg SSSR-a. Korištenje njihovog potencijala će podrazumijevati brodski transport CO₂ do tih regija; što u suštini smanjuje njihov ekonomski potencijal. Ukupni iskoristivi kapacitet spremanja u iscrpljena ležišta prirodnog plina se procjenjuju na 1 000 Gt CO₂ i odgovara svjetskoj emisiji od 50-ak godina.

Ovo je vrlo gruba teoretska procjena kapaciteta iscrpljenih ležišta, stvarni potencijal može biti bitno reduciran prirodnim zavodnjavanjem (potapanjem) i nemogućnošću postizanja izvornog tlaka ležišta.

Važno je napomenuti da je odlaganje u iscrpljena i napuštena ležišta nafte i prirodnog plina (uključujući i opcije povećanja iscrpka aktivnih ležišta) osjetno manji rizik nego spremanje u duboke slane vodonosnike, budući da je geologija vodonosnika često velika nepoznanica.

5.3 Odplinjavanje ležišta ugljena od metana

Povećanje iscrpka metana (ugljeni plin) iz ležišta ugljena je spekulativna metoda. Kod konvencionalnog iskorištenja metana iz ležišta ugljena se može postići 40 % do 50 % iscrpka u neposrednoj blizini bušotine, dok se u slučaju utiskivanja CO₂ iscrpak teoretski može povećati na 90 % do 100 %. ECBM je ograničen na ležišta ugljena koja nije moguće eksploatirati ili nisu tehno-ekonomski isplativa, što je glavni izvor neizvjesnosti koji ovisi o razvoju rudarske tehnologije i energetskih potreba. ECBM se može primijeniti u ležištima ugljena dovoljne propusnosti. Porastom tlaka, adsorpcija CO₂ raste od 2 mola/mol u metana na 700 m na 5 mola/mol u na 1 500 m. Rezerve ugljena ne smiju biti na dubinama većim od 2 000 m jer porast temperature ograničava sadržaj metana u ugljenu, a porast tlaka na većim dubinama

tion of natural methane and increase of pressure in the deposit. Until 2007, injection of CO₂ has not been used for commercial purposes. It is not certain whether the application of this method is justified. It all depends on the time necessary for CO₂ to reach the gas deposit. The capacity of CO₂ storage in gas deposits is estimated to be of larger potential than the possibility of storage into oil deposits. Technological-economical justifiability analyses of many projects determined much lesser income (e.g. about 1,8 GJ of natural gas is obtained by injection of one ton of CO₂) than at injection into oil deposits.

5.2 Storage in depleted oil or natural gas deposits

The storage activity is quite simple because only injection boreholes need to be constructed (depending on the field geology and the injection speed). Most of the existing infrastructure can be used and this significantly reduces the investments. The storage capacity will grow in the future because the number of depleted oil and gas deposits will grow, particularly in the Middle East and the former USSR countries. The use of the potential thereof will require ship transport of CO₂ to those regions; this basically reduces their economic potential. Total useful capacity of storage into depleted natural gas deposits is estimated at 1 000 Gt CO₂ and this equals some 50 years of world emission.

This is a very rough theoretical estimate of the depleted deposits' capacity; actual capacity may be significantly reduced by natural inundation (flooding) and by the inability to achieve the original deposit pressure.

It is important to mention that disposal into depleted and abandoned oil and natural gas deposits (including the options of increase of active deposit extraction ratios) bears significantly less risk than storage into deep saline aquifers, as the geology of the aquifers is often a great unknown.

5.3 Coal seams methane degassing

Enhanced methane (coal gas) extraction from coal seams is a speculative method. At conventional exploitation of methane from coal seams, in the direct vicinity of the borehole, 40 % up to 50 % can be obtained, while in the case of injection of CO₂, the extraction ratio can theoretically rise to 90 % up to 100 %. ECBM is limited to coal seams which cannot be exploited or which are not technologically-economically cost-effective. This is the main source of uncertainty and it depends on the development of mine technology and energy requirements. ECBM can be applied in coal seams of sufficient permeability. By increase of pressure, the CO₂ adsorption increases from 2 mol/ 1 mol of methane at 700 m to 5 mol/1 mol methane at 1 500 m. Coal reserves must not be

smanjuje propusnost ležišta. Sadržaj metana u dubokim ležištima može varirati od $5 \text{ m}^3/\text{t}$ do $25 \text{ m}^3/\text{t}$ ugljena ovisno od debljine sloja (i ostalim značajkama), tako da ECBM potencijal po bušotini i troškovima spremanja CO_2 varira s faktorom pet i više. To znači da su najatraktivnije opcije s gledišta iscrpka metana - plitke rezerve ugljena debelog sloja, ali one često ne ispunjavaju temeljne kriterije eksploatacije.

Selekcija ležišta ugljena za ECBM se mora temeljiti na kriterijima kao što su:

- homogena rezerva,
- poprečna i vertikalna izoliranost od okolnih slojeva,
- minimalna ispresijecanost rasjedima i naborima,
- propusnost minimalno od, $1 \times 10^{-15} \text{ m}^2$ do $5 \times 10^{-15} \text{ m}^2$, većina ugljenih ležišta su mnogo manje propusnosti.

Kriterije prema iskustvenim procjenama zadovoljava manji broj potencijalnih ležišta. Visoki sadržaj metana, stratigrafički koncentriranog ležišta je u prednosti nad višeslojnim ležištem. Mogućnost iskorištenja ili eksport metana cjevovodom kao i raspoloživost CO_2 (lokalne termoelektrane, industrija ili magistralni cjevovodi za CO_2) pozitivno utječu na selekciju ležišta. Svjetski potencijal spremanja u duboka neeksploatabilna ležišta ugljena se procjenjuje na 150 Gt CO_2 . Analize pokazuju da samo 5 Gt CO_2 do 15 Gt CO_2 ECBM projekata pokazuje moguću profitabilnost, dok oko 50 Gt kapaciteta može biti korišteno s umjerenim troškovima spremanja, ispod 50 USD/t CO_2 , u koje nisu uključeni troškovi hvatanja i transport (IEA GHG Programme, 1998). Uz pretpostavku da 2 mola CO_2 zamjenjuje jedan mol metana, utisnutih 10 Gt CO_2 odgovara energiji od 90 EJ ($\text{E} = \text{eksa} = 10^{18} = \text{trilijun}$) sadržanoj u prirodnom plinu potrošenom tijekom jedne godine u svijetu! Masovnije iskorištenje ECBM tehnologije se zbog toga trenutačno smatra fikcijom u realnom elektroenergetskom sektoru.

Ugljen je sklon bubrenju u kontaktu s CO_2 što ima za posljedicu redukciju propusnosti. Niska propusnost, u nekim slučajevima, može biti nadjačana pucanjem formacije sloja ugljena. Trošak izgradnje bušotina za utiskivanje ekspencijalno raste s dubinom ležišta ugljena; koso bušenje je 70% skuplje od vertikalnog bušenja. Velika gustoća utisnih bušotina je presudno potrebna za ECBR. Troškovi utisnih bušotina predstavljaju $\frac{3}{4}$ ukupnih troškova. Vrlo teško je generalno odrediti ukupne troškove za velike razmjere primjene, budući da osjetno variraju od slučaja do slučaja. Veliki broj bušotina dodatno smanjuje upotrebljivost zemljišta. Kod plitkih nalazišta ugljena pojava i problem dreniranja vode

at depths exceeding 2000 m because the increase of temperature limits the content of methane in the coal, and the increase of pressure at greater depths reduces deposit permeability. Methane content in deep deposits may vary from $5 \text{ m}^3/\text{t}$ up to $25 \text{ m}^3/\text{t}$ of coal, depending on layer thickness (and other properties) and therefore the ECBM potential per borehole and CO_2 storage costs vary with a factor of 5 or more. This means that the most attractive options, from the aspect of the methane extract, are shallow thick-layer coal reserves but these often do not meet the basic exploitation criteria.

Selection of coal seams for the ECBM must be based on criteria such as:

- homogenous reserve,
- transverse and vertical isolation from the surrounding layers,
- minimal intersection by faults and folds,
- permeability of at least $1 \times 10^{-15} \text{ m}^2$ up to $5 \times 10^{-15} \text{ m}^2$, most coal deposits are of significantly lesser permeability.

According to experiential estimates, only a small number of potential deposits meets the criteria. High methane content of a stratigraphically concentrated deposit is preferable to the multi-layer deposit. The possibility of exploitation or export of methane by pipelines as well as the availability of CO_2 (local thermal power plants, industry or main CO_2 pipelines) positively impact the deposit selection. The global potential of storage into deep non-exploitable coal seams is estimated at 150 Gt CO_2 . Analyses show that only 5 Gt CO_2 up to 15 Gt CO_2 of ECBM projects show potential profitability, while about 50 Gt of the capacity can be used with moderate storage costs lower than 50 USD/t CO_2 and exclusive of capture and transportation costs (IEA GHG Programme, 1998). Under the presumption that 2 mol of CO_2 substitute one mol of methane, injected 10 Gt CO_2 equal the energy of 90 EJ contained in natural gas used in a year throughout the world! Mass exploitation of the ECBM technology is therefore currently not viewed as fictive in the real electric power sector.

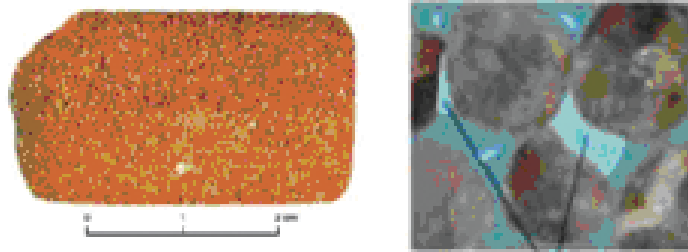
Coal tends to expand in contact with CO_2 which results in reduced permeability. Low permeability, in some cases, can be overcome by a burst of the coal layer formation. The cost of construction of injection boreholes increases exponentially with the depth of the coal deposit; diagonal drilling is by 70% more expensive than vertical drilling. High density of injection boreholes is decisively necessary for the ECBR. Costs of injection borehole represent $\frac{3}{4}$ of total costs. It is very hard to determine generally the total costs for wide application scopes because they vary significantly from case to case. A large number of boreholes further reduces land exploitability. With shallow coal deposits, the occurrence

iz slojeva ugljena može prouzročiti tonjenje tla, a kod dubokih ležišta problem zbrinjavanja slane vode može biti naglašen. Današnji pilot projekti ECBM se nalaze u SAD i Kanadi, a treći je u razradi, u Poljskoj. Dosadašnji rezultati nisu dovoljno uvjerljivi i smatraju se nedovoljnim za generalne zaključke vezane za dalji razvoj komercijalizacije ECBM. Studija za projekt ECBM u Nizozemskoj pretpostavlja specifičnu cijenu transporta i spremanja u rasponu od 50 USD/t CO₂ do 75 USD/t CO₂ bez troškova hvatanja i izdvajanja i to pri cijeni plina od 3,5 USD/GJ.

Zaključiti se može da je tehnologija ECBM u ranoj stupnju razvoja, tako da je njena perspektiva još uvijek neizvjesna. Po realizaciji nekoliko većih razvojnih projekata moći će se nakon njihove višegodišnje eksploatacije dati meritorna ocjena o njihovoj sigurnosti i okolišnoj prihvatljivosti. U većini slučajeva će dobit biti limitirana gubitcima zbog nepredvidivih dodatnih troškova.

5.4 Spremanje u duboki slani vodonosnik

Slani vodonosnik je sloj sedimentnih stijena, zasićenih vodom, u koje se može ukoliko su zadovoljavajuće poroznosti utiskivati fluid. Porozni vodonosnici čvrste spužvaste strukture su prikazani na slici 4. Karbonatne stijene su obično vodonosnici zadovoljavajuće poroznosti.



Slika 4 — Pješčenjak duljine 2 cm (lijevo) i karbonatna stijena (desno) [10]
Figure 4 — 2-cm long sandstone (left) and carbonate rock (right) [10]

Voda zadržana milijunima godine u porama i pukotinama stijena sadrži visoku koncentraciju otopina, obično je to slana voda neprikladna za piće. Kristalno i metamorfno kamenje, poput granita, nema potrebnu poroznost za skladištenje CO₂, ali ukoliko se nalazi iznad sloja pješčenjaka, funkcionira kao prirodno brtvilo. Otvoreni i uski vodonosnici nemaju prirodnih barijera za strujanje vode, tako da se odvija spora prirodna cirkulacija i nažalost nisu podobni za skladištenje CO₂.

U Norveškoj se na plinskom ležištu Sleipner, separirani CO₂ skladišti u slani vodonosnik ispod

and the problem of draining water from coal layers can cause soil sinking, and in deeper layers, the problem of disposal of saline water could be pronounced. Today's ECBM pilot projects are located in the USA and Canada and the third is being elaborated in Poland. Results so far are not convincing enough and are considered insufficient to make general conclusions for the further development of ECBM commercialization. The study for the ECBM project in the Netherlands presumes the specific transport and storage price in the range between 50 USD/t CO₂ up to 75 USD/t CO₂ exclusive of capture and isolation costs and that being at the price of gas of 3,5 USD/GJ.

The conclusion can be drawn that the ECBM technology is at an early phase of development, so that its perspective is still uncertain. After the implementation of a few larger projects and several years of exploitation, a merit-based assessment of their safety and environmental acceptability will be made. In most cases, the profit will be limited by losses due to unpredicted additional costs.

5.4 Storage in deep saline aquifers

A saline aquifer is a layer of water-protected sedimentary rocks into which fluid can be injected if they are of adequate porosity. Porous aquifers of solid spongy structure are shown in Figure 4. Carbonate rocks are usually aquifers of adequate porosity.

Water which has been kept for millions of years in pores and crevices contains a high concentration of solvents and this is usually saline water unsuitable for drinking. Crystal and metamorphic stones, such as granite, do not have the necessary porosity for the storage of CO₂, but if located above the sandstone layer, they operate as natural sealants. Open and narrow aquifers do not contain natural barriers for water flow, so that slow and natural circulation takes place and thus these are unfortunately not adequate for storage of CO₂.

In Norway, in the Sleipner gas deposit, the separated CO₂ is stored in the saline aquifer under the gas

plinskog ležišta. Skladišti se oko 1 Mt CO₂ godišnje od 1996. godine. Skladištenje je tehnički potpuno opravdano. Uočena su očekivana kretanja ugljikovog dioksida prema površini, a propuštanja nisu uočena. Specifična investicija (komprimiranje i utiskivanje) je iznosila 80 USD/t CO₂. Nije moguće niti nakon niza ispitivanja točno procijeniti potencijal skladištenja (potencijal preostalih slobodnih pora). Konzervativne procjene su se kretale oko 2 % kapaciteta jedinice volumena, ali su kasnija istraživanja pokazala da bi se moglo uz niže troškove iskoristiti između 13 % i 68 % jedinice volumena pravilnim odabirom rasporeda i broja bušotina. Novi Norveški projekt Snøhvit (komprimiranje, transporta i utiskivanje) je procijenjen na 275 USD/t CO₂, najveći udio ulaganja se odnosi na komprimiranje i transport, specifično visoka ulaganja su određena lokacijom spremnika i pogonskim iskustvom. Bez značajnih subvencija projekt neće moći biti realiziran.

Ugljikov dioksid se u dubokom slanom vodonosniku sprema na nekoliko načina [10]:

- u obliku peraste strukture, plinovite perjanice na vrhu vodonosnika, slično akumulaciji nafte ili plina ispod brtveće kape nepropusnih stijena, čije rasprostiranje traje preko 1 000 godina (!) i to obično pet do dvanaest kilometara od utisne bušotine (pouzdanost matematičkog modela predviđanja je dvojben),
- kao mjehurići zarobljeni u prostoru pora nakon prolaska glavne protoka,
- otapanjem u slanom vodonosniku poput šećera u čaju,
- kao istaloženi karbonatni mineral nastao geokemijskim reakcijama između CO₂, vode iz vodonosnika i stijena.

Brojne studije su pokazale da se tijekom utiskivanja CO₂, do 30 % CO₂ otapa u slanoj vodi. Budući da je CO₂ lakši od slane vode, preostali CO₂ će plivati na vrhu slane vode i postupno se akumulirati. Kasnije se dio akumuliranog CO₂ otapa ili reagira s okolnim stijenama. Perasta struktura iznad vodonosnika se otapa više od tisuću godina! Značajniji efekti geokemijskih reakcija, zbrinutog CO₂, se uočavaju nakon nekoliko tisuća godina. Gdje nema stratigrafske ili strukturne zamke CO₂ se širi, prema matematičkim modelima, na velike površine i to desetinama i stotinama kvadratnih kilometara (!) ovisno o debljini slanog vodonosnika, poroznosti i propusnosti, reljefa brtveće kape i utisnutog volumena. Praćenje i utvrđivanje propuštanja spremljenog CO₂ u slani vodonosnik je veoma složeno. Spekulativna opcija je injektiranje pripremljene otopine CO₂ u slanoj vodi tako da bi se izbjegla mogućnost stvaranja peraste strukture. Procjene potencija-

deposit. About 1 Mt CO₂ have been stored annually since 1996. The storage is technically completely justified. Expected flows of carbon dioxide towards the surface have been observed and no leakages. The specific investment (compression and injection) amounted to 80 USD/t CO₂. Even after several tests, it is impossible to estimate accurately the storage potential (the potential of the remaining free pores). Conservative estimates fluctuated at about 2 % of volume unit capacity but later research showed that with lower costs, between 13 % and 68 % of volume units could be used under the condition that the right number and arrangement of boreholes were chosen. The new Norwegian project of Snøhvit (compression, transport and injection) is estimated at 275 USD/t CO₂; the largest part of the investment relates to compression and transportation, and specifically high investments are conditioned by the location of the reservoir and the experience of the operation. Without significant investment, it will be impossible to realize the project.

In the deep saline aquifer, carbon dioxide is stored in several ways [10]:

- in a feather-structured form, gas plume at the top of the aquifer, similar to oil or gas accumulation under the sealing cap of non-porous rocks, and their spreading lasts over 1 000 years (!) and that usually being five to twelve kilometres from the injection borehole (the reliability of the mathematical prediction model is uncertain),
- as bubbles captivated in the pore space after the passage of the majority of the flow,
- by solution in the saline aquifer like sugar in tea,
- as settled carbonate mineral arising from geochemical reactions between CO₂, water from aquifers and rocks.

Numerous studies have shown that at injection of CO₂, up to 30 % CO₂ dissolves in saline water. As CO₂ is lighter than saline water, the remaining CO₂ will float on top of the saline water and gradually accumulate. Later on, part of the accumulated CO₂ dissolves or reacts with the surrounding rocks. The feathery structure above the aquifer dissolves for more than a thousand years! More significant effects of geochemical reactions of the disposed CO₂ are visible after several thousand years. Where there is no stratigraphic or structural trap, CO₂ spreads, according to mathematical models, onto large surfaces and that for tens and hundreds of square kilometres (!) depending on the thickness of the saline aquifer, the porosity and the permeability, the sealant cap relief and the injected volume. The supervision and determining of the leakage of the CO₂ stored in the saline aquifer is very complex. A speculative option is the injection of the prepared solution of CO₂ in the saline water so as to avoid

la skladištenja CO₂ u duboke slane vodonosnike oscilira ovisno o metodologiji, podacima i ostalim čimbenicima i kreće se do 10 000 Gt.

Temperaturni profil podzemnih sedimenata je veoma različit po lokacijama, jer oscilira geotermalni gradijent i temperatura površine stijena u dubokim slojevima. Stanje CO₂ pod zemljom će varirati i biti određeno gustoćom pri lokalnom tlaku. To utječe na potencijal skladišta po jedinici površine i određuje mehanizam propuštanja.

Iz ugljenom ložene termoelektrane električne snage od 500 MW treba spremati oko 3 000 kt CO₂ po godini. Uz pretpostavku da CO₂ gustoće 0,5 t/m³ može biti spremljen u slani vodonosnik pri njegovoj efektivnoj debljini od 1 metra, tijekom jedne godine pogona elektrane je potrebno 6 km² slanog vodonosnika za skladištenje emisije CO₂. Tijekom životnog vijeka od 40 godina potrebna je površina od 240 km² za skladištenje CO₂. Za spremanje emisije od 16 Gt CO₂ godišnje, oko 60 % godišnje svjetske emisije, je potrebno osigurati skladište površine poput Nizozemske.

5.5 Druge mogućnosti skladištenja u elektroenergetskom sektoru

Predlažu se brojne opcije skladištenja od kojih je jedino vrijedno napraviti kratak osvrt, prema procjeni autora članka, na spekulativne mogućnosti skladištenja u kupke vapnenca, površinsku mineralizaciju i skladištenje u oceane. Navedene mogućnosti skladištenja su generalno po opsegu angažiranja stvari za proces izvanredno zahtjevne, imaju vrlo veliku vlastitu potrošnju, mogućnost nadzora kroz tisuće godina je dvojbena kao i saniranje mogućih poremećaja u spremnicima.

Koncept vapnenačkih kupki je kombinacija hvatanja i spremanja. Kroz kupku, u kojoj je vapnenac otopljen u vodi, struje dimni plinovi iz kojih ugljikov dioksid reagira s vapnencem. Preliminarne procjene, iz više izvora informacija, ukupni trošak hvatanja i spremanja procjenjuju na oko 25 USD/t CO₂. Ovaj proces nije u dovoljnoj mjeri provjeren na pilot postrojenjima. Veći broj stručnjaka je uvjeren da je nemoguće proizvesti dovoljno male mjehuriće dimnog plina, potrebna je izuzetno velika površina reakcije, jer je transport CO₂ kroz otopljeni karbonat ograničavajući faktor te da će i velike dimenzija kupke vapnenca (smještaj opreme) biti limitirajući faktor.

Koncept površinske mineralizacije se temelji na reakciji magnezija iz tla i/ili kalcija silikatnih/eruptivnih stijena s CO₂ u karbonate. Slabo kiselina otopina CO₂ u slanoj vodi može reagirati s mineralima okolnih stijena stvarajući navlake novih minerala. Brzinu procesa određuje kemijski sastav stijena i voda. Značajna količina stvari je

the possibility of formation of the feathery structure. Estimate of the potential for the storage of CO₂ in deep saline aquifers oscillates depending on the methodology, data and other factors and fluctuates up to 10 000 Gt.

The temperature profile of the underground sediments varies significantly from location to location because the geothermal gradient and the temperature of the rock surface in deep layers oscillate. Underground CO₂ states will vary and be determined by the density at local pressure. That affects the storage potential per surface unit and determines the leakage mechanism.

From a coal-fired thermal power plant of 500 MW (electric) about 3 000 kt CO₂ should be stored per year. Under the presumption that CO₂ with the density of 0,5 t/m³ can be stored in deep saline aquifers at its actual thickness of 1 metre, during one year of the power plant's operation, 6 km² of saline aquifer are necessary for storage of the CO₂ emission. During a life cycle of 40 years, a surface of 240 km² is necessary for the storage of CO₂. For the storage of the emission of 16 Gt CO₂ per year, which is about 60 % of the annual world emission, it is necessary to ensure room for storage with the surface as great as the Netherlands.

5.5 Other storage options in the electric power system

Numerous options are suggested of which the only that are worth the observation, according to the judgement of the author of the article, are the speculative options of storage in limestone baths, superficial mineralization and storage in oceans. The above storage options are generally, according to the scope of substance employment for the process, extremely demanding, have very high own consumption, the possibility of supervision over thousands of years is uncertain as well as the restoration of possible disruptions in the reservoirs.

The limestone bath concept is a combination of capture and storage. Flue gases circulate through the bath, in which the limestone is dissolved in water, and the carbon dioxide from these gases reacts with the limestone. Preliminary estimates, from several data sources, set the total capture and storage cost at about 25 USD/t CO₂. This process has not been tested enough on pilot plants. Many experts are convinced that it is impossible to produce flue gas bubbles which are small enough, and that an extremely large reaction surface is necessary because the CO₂ transport through the dissolved carbonate is a limiting factor and that large limestone bath dimensions (equipment location) will also be a limiting factor.

The superficial mineralization concept is based on the reaction of the magnesium from the ground and/

uključena u proces, npr. uklanjanje CO₂ iz ugljenom loženog bloka električne snage od 500 MW proizvodi 30 kt magnezijevog karbonata tijekom dana (oko 1 000 kamiona!). Egzotermni proces vezivanja je testiran samo laboratorijski. Određeni tipovi podobnih eruptivnih stijena (obično nisu u sedimentima ležišta iz kojih se vade fosilna goriva) su razbacani širom svijeta, a sadrže 40 % do 50 % MgO i CaO. Za spremanje jedne tone CO₂ treba 0,9 t MgO; pri čemu se stvara oko 2,8 t otpada. Glavna zapreka, iz inženjerske perspektive gledano, je kinetika reakcije. Niti jedan tehnološki proces površinske mineralizacije nije koncipiran na stvarnim brzinama reakcije. Kruti otpad, koji se stvara u velikim količinama je potrebno ukloniti iz procesa i obraditi prije zbrinjavanja; razmjeri pothvata su poput izgradnje piramida u Egiptu. Očekivanja komercijalne primjene se temelje na procjenama spremanja od 30 USD/t CO₂ (hvatanje i transport su isključeni). Potrebno je optimirati troškove transporta silikatnih materijala do izvora emisije CO₂ ili lokacije spremanja. Proces je interesantan ukoliko ne postoje druge mogućnost uskladištenja. Neki stručnjaci smatraju da tehnološki proces nema budućnosti, osim možda nekih modificiranih postupaka temeljenih na otpadnom građevinskom betonu. Nepouzdan optimum procesa površinske mineralizacije se postiže pri tlaku od 1 bar i temperaturi od oko 350 °C, premda treba izvesti još niz opita (kinetika, katalizatori itd.)

Skladištenje CO₂ u oceane je kontraverzna opcija koja može biti provedena:

- otapanjem u morskoj vodi i spremanjem CO₂ u obliku hidrata i
- spremanjem tekućeg CO₂ na morske dubine veće od 4 000 m.

Većina tehnoloških postupaka uskladištenja na velikim dubinama oceana je provjerena u praksi. Međutim, vrlo malo je poznat utjecaj porasta koncentracije CO₂ na ekosustav oceana. Pilot projekti na Havajima i u Norveškoj su otkazani zbog prosvjeda ekologa. Japan smatra da bi opcija zbrinjavanja u oceane bila za njih poželjna, budući da ne raspolažu dovoljnim kapacitetom spremanja CO₂ u tlo. Rezultati proračuna matematičkim modelima navode da bi 80 % do 90 % spremjenog CO₂, na dubini od 3 000 m, trebalo biti trajno zadržano u oceanima za više od 500 godina. Na dubinama od 1 000 m zadržano bi bilo 30 % do 80 % spremjenog CO₂. To znači da dubina skladišta određuje količinu oslobođenog i reapsorbiranog CO₂ u atmosferu. Istjecanje CO₂ iz nedovoljno dubokih spremnika izravno utječe na ekosustav oceana kroz promjenu kiselosti vode, što se smatra glavnom preprekom. Morala bi se neutralizirati karbonska ki-

or calcium of the silicate/eruptive rocks with CO₂ in the carbonates. In saline water, the mildly acid CO₂ solution may react with the minerals of the surrounding rocks creating new mineral casings. The speed of the process is determined by the chemical composition of rocks and water. The process includes a number of substances, for example, the removal of CO₂ from the coal-fired block with the power of 500 MW produces 30 kt of magnesium carbonate during one day (about 1 000 trucks!). The exothermal bonding process has undergone laboratorial tests only. Certain types of eligible eruptive rocks (these are usually not in the sediments of the deposits from which fossil fuels are extracted) are dispersed all over the world and contain 40 % up to 50 % of MgO i CaO. The storage of one ton of CO₂ requires 0,9 t MgO; whereat about 2,8 t of waste is generated. The main obstacle, viewed from the engineering perspective, is reaction kinetics. None of the technological processes of superficial mineralization are conceived on actual reaction speeds. Crude waste, which is generated in large quantities, needs to be removed from the process and analysed before disposal; proportions of the project are like the construction of the pyramids of Egypt. Commercial application expectations are based on storage estimates of 30 USD/t CO₂ (exclusive of capture and transport). Silicate materials transport costs should be optimized up to the CO₂ emission source or to the storage location. The process is interesting if there are no other storage options available. Some experts believe that the technological process has no future, except maybe for some modified procedures based on waste construction concrete. The unreliable optimum of the superficial mineralization process is achieved at the pressure of 1 bar and a temperature of about 350 °C, however, several more tests still need to be undertaken (kinetics, catalysts, etc.).

Storage of CO₂ in oceans is a controversial option which can be performed:

- by dissolution in saline water and storage of CO₂ in the form of hydrates and
- by storage of liquid CO₂ at sea depths greater than 4 000 m.

Most technological storage processes at great ocean depths have been tested in practice. However, the impact of increased CO₂ concentration on the ocean ecosystem is slightly known. Pilot projects in Hawaii and in Norway were cancelled due to environmentalists' protests. Japan believes that the option of storage in oceans would be desirable for them because they do not avail of sufficient capacities for the underground storage of CO₂. Results of calculations by virtue of mathematical models state that 80 % up to 90 % of stored CO₂ at the depth of 3 000 m should be permanently kept in oceans for more than 500 years. At the depths of 1 000 m, 30 % up to 80 % of stored CO₂ would be kept permanently. That means

selina vapnencem ili nekim drugim kemijskim dodatkom (baferom), jer bi u protivnom dodatne tisuće gigatona ugljika u oceanima proizvodilo značajne kemijske smetnje velikih razmjera. Nužna su dalja istraživanja radi boljeg razumijevanja procesa spremanja CO₂ u dubokim oceanskim vodama.

6 TRAJNOST I POUZDANOST SPREMNIKA I NADZOR

Dva tipa rizika su vezana za propuštanje CO₂ spremnika: lokalni specifičan za zdravlje, sigurnost i okoliš, te globalni vezan za vraćanje spremljenog CO₂ u atmosferu. Uzme li se u razmatranje samo globalni rizik, čini se da bi propuštanje do 0,1 % godišnje bilo prihvatljivo. Ono bi trebalo biti gornja granica u dozvoli za pogon; tehnička struka očekuje u stvarnim uvjetima rada daleko manja propuštanja. Vrlo veliki broj iznenađenja je moguće od spremljenog ugljikovog dioksida, promjene su vrlo spore, teško uočljive, a još teže ih je zaustaviti [11]. 20 % do 30 % veća koncentracija od normalne je fatalna za faunu. Prirodna katastrofa izbijanja ugljikovog dioksida nakon potresa i vulkanskih erupcija mogu biti indikativna i za incidente na sustavima HITS CO₂. Za zagađenje s CO₂ indicije su kod podzemnih voda smanjivanje PH vrijednosti, pojava teških metala u vodi za piće, kontaminacija površinskih voda, oksidacija osjetljivih tvari, i slično. Podzemni spremnici CO₂ mogu inicirati vrlo nepovoljne seizmičke aktivnosti slične onima kod sezonskih spremnika prirodnog plina. Velika su nepoznanica propuštanja brtvi (od cementa) na spremnicima CO₂. Mineralne vode koje izbijaju iz slanah vodonosnika reduciraju vrijeme zadržavanja spremljenog CO₂ [9] sa 7 000 godina na 2 000 godina. Potrebno je mnogo više pokusnih postrojenja za potpuniju procjenu trajnosti spremanja i to naročito za odlaganje u duboke slane vodonosnike. Nužan je i razvoj kriterija odabira lokacija, prije nego bude bilo moguće nominirati neku od njih i utvrditi odgovarajuće postupke trajnog nadzora nad skladištem. Ukoliko bi bio stabiliziran (dogovorom) limit koncentracije na 450 ppmv CO₂ u atmosferi, s ciljem njegovog održavanja, ugljikov dioksid bi trebalo zadržati oko 7 000 godina u spremnicima, dobiven iz preostalih rezervi ugljena i to uz prihvatljivo propuštanje [2].

Spremnike s pohranjenim ugljikovim dioksidom je nužno nadzirati stotinama, a u nekim slučajevima i tisućama godina zbog spore geokemijske reakcije. Sljedeće teme povezane s faktorom rizika su predmet istraživanja:

that the storage depth determines the quantity of CO₂ released and re-absorbed into the atmosphere. Leakage of CO₂ from insufficiently deep reservoirs directly impacts the ocean ecosystem through the change of water acidity and this is considered to be the greatest obstacle. Carbonic acid should be neutralized by limestone or some other chemical adjuvant (buffer) because, in the contrary, additional thousands of gigatons of carbon in the oceans would produce significant and extensive chemical disruptions. Further research is necessary for the purpose of better understanding of the process of storage of CO₂ into deep ocean waters.

6 DURATION/RELIABILITY OF THE RESERVOIR AND ITS SUPERVISION

Two types of risks are related to CO₂ reservoir leakage: local, related to health, safety and the environment, and the global, related to the return of the stored CO₂ into the atmosphere. If only global risk is taken into observation, it seems that annual leakage of up to 0,1 % would be acceptable. It should be the top limit in the operation permit; in actual working conditions, the technical profession expects far less leakage. Many surprises are possible to happen with stored carbon dioxide; changes are slow, hardly visible and even harder to be stopped [11]. A concentration higher by 20 % up to 30 % than normal is fatal for the fauna. The natural disaster of carbon dioxide bursts after earthquakes and volcano eruptions could be indicative for CITS CO₂ system incidents as well. In underground waters, reduced PH value, presence of heavy metals in drinking water, contamination of surface waters, oxidation of sensitive substances, etc. indicate CO₂ pollution. Underground CO₂ reservoirs may initiate very unfavourable seismic activities similar to those in seasonal natural gas reservoirs. Sealant (made of concrete) leakages on CO₂ reservoirs are an unknown. Mineral waters which emerge from the saline aquifers reduce the time the stored CO₂ is kept [9] from 7 000 years to 2 000 years. Many more test plants are necessary to make a fuller estimate of storage permanency and that particularly for disposals into deep saline aquifers. The development of the location selection should be undertaken before some of them can be nominated and adequate procedures of constant storage supervision can be determined. If the concentration limit is to be stabilized (by agreement) at 450 ppmv CO₂ in the atmosphere, for the purpose of its maintenance, carbon dioxide should be kept for about 7 000 years in the reservoirs. The carbon dioxide should be gained from the remaining coal reserves and the leakage should be acceptable [2].

Reservoirs with stored carbon dioxide have to be supervised for hundreds, and, in some cases, for tho-

- studiranje fizikalnih i kemijskih procesa u spremnicima,
- postupci i kriteriji odabira ležišta, uključujući i analize seizmičkih aktivnosti,
- metode predskazivanja dugoročnog ponašanja CO₂ u podzemlju,
- tehnike i metode nadgledanja i provjere,
- procjene rizika i upravljanje rizicima,
- postupci i normativi sigurnosti,
- integritet ispravnosti bušotina.

Nameće se zaključak da su tehnološki postupci hvatanja i izdvajanja bliži komercijalizaciji od postupaka skladištenja i nadzora nad skladištima, jer je kod njih daleko veći broj nedovoljno istraženih korelacija koje bitno utječu na sigurnost uskladištenog ugljikovog dioksida.

7 PROIZVODNJA GORIVA I KEMIJA IZ CO₂

Na prvi pogled izgleda da ne bi mogla zaživjeti proizvodnja goriva za transportna sredstva iz CO₂. Međutim, zasada samo iz energetske perspektive, smisla ima ako na jednoj lokaciji postoji višak čiste energije proizvedene iz nuklearnih ili obnovljivih izvora, a na drugoj postoji potreba za energijom. CO₂ bi se tada transportirao brodovima iz jedne regije u drugu, dok bi se ugljikovodična goriva (metanol i dimetil eter - DME) transportirala u suprotnom pravcu. Obnovljivi izvor ugljika, poput biomase, je potreban za proizvodnju metanola i DME koji su znatno jeftiniji od vodika ili elektro-akumulatora namijenjenih transportu. Trenutačno ne postoje na tržištu plinske turbine koje mogu u dugotrajnom pogonu spaljivati čisti vodik. Problem su visoka lokalna naprezanja materijala glavnih komponenti izloženih plamenu vodika.

Značajnom smanjenju ukupne emisije CO₂ može doprinijeti proizvodnja metanola i DME iz recikliranog CO₂ (uhvaćen i izdvojen) iz dimnih plinova tijekom spaljivanja biomase:
 $CO_2 + 3H_2 \rightarrow CH_3OH$.

Ako se metanol koristi za proizvodnju transportnih goriva, tada je redukcija emisije CO₂ oko 3,14 t po 1 Gt supstituiranog goriva za transport. Po toni metanola je potrebno uložiti 28 GJ električne energije! Očito su u pitanju vrlo skupa goriva za koja bi trebalo provjeriti opravdanost masovne proizvodnje.

usands of years because of the slow geochemical reaction. The following subjects related to the risk factor are the subject of research:

- studying physical and chemical processes in the reservoirs,
- procedures and criteria for choice of deposits, including the analyses of seismic activities,
- long-term CO₂ underground behaviour prediction methods;
- supervision and control techniques and methods,
- risk assessments and risk management,
- safety procedures and standards,
- borehole operation integrity.

The conclusion seems to be that technological capture and isolation procedures are much closer to commercialization than the storage and storage supervision procedures because they include a much larger number of insufficiently researched correlations which significantly impact the safety of the stored carbon dioxide.

7 PRODUCTION OF FUEL AND CHEMICALS FROM CO₂

At first glance, it seems that production of fuel from CO₂ for means of transportation could not take hold. However, for now only from the energy perspective, it makes sense only if in one location there is excessive pure energy produced from nuclear or renewable sources and if in the other location there is a need for energy. CO₂ would then be transported by ships from one region to another, while hydrocarbon fuels (methanol and dimethyl ether - DME) would be transported in the opposite direction. A renewable coal source, such as biomass, is necessary for the production of methanol and DME which are much cheaper than hydrogen or electric accumulator batteries intended for transport. At the moment, there are no gas turbines on the market which can, in long-term operation, burn pure hydrogen. The problem are high local stresses of the materials of the main components exposed to hydrogen flames.

The production of methanol and DME from recycled CO₂ (captured and isolated) from flue gases during the burning of biomass can contribute to a significant reduction of the total emission of CO₂:
 $CO_2 + 3H_2 \rightarrow CH_3OH$.

If methanol is used for the production of transport fuels, then the CO₂ emission reduction is about 3,14 t per 1 Gt of substituted transport fuel. Per one ton of methanol, 28 GJ of electricity need to be put in! The issue at hand are obviously expensive fuels for which the justifiability of mass production should be verified.

8 TROŠKOVI HITS-a

Pouzdanih procjena o ukupnim troškovima HITS-a kao i o pojedinim troškovima tehnološkog lanca nema. Većina tehnologija nije provjerena na demonstracijskim postrojenjima velikih jediničnih kapaciteta, već je samo pokazano njihovo zadovoljavajuće funkcioniranje na pilot postrojenjima (tablica 5).

Europska unija ima uspostavljen sustav trgovanja emisijskim jedinicama stakleničkih plinova (EU-ETS), u okviru kojeg se utvrđuju dopuštene razine emisija za industrije i uspostavlja sustav trgovanja emisijskim dozvolama. Cijena emisijske dozvole na tržištu je iznosila oko 15 EUR/t u prosincu 2008. godine. Pri ovakvoj cijeni dozvola za emisiju, ne isplati se aktivirati projekte izgradnje HITS-a, jer isti nisu ekonomski samoodrživi. Trenutačno se može vrlo grubo, zbog velikog broja opcija, procijeniti da bi ukupni trošak HITS tehnologije bio unutar 50 USD/t CO₂ do 100 USD/t CO₂ smanjenog emitiranja. Sve dok ne bude postignuta ekonomska samoodrživost HITS-a nužni će biti financijski poticaji. Prije početka krize globalnog gospodarstva, koncem 2008. godine Europska unija je imala nacrt prijedloga plana ulaganja u energetiku reda veličine 200 milijardi eura do 2030. godine. Ista bi bila, uz utjecaje na druge tržišne mehanizme, usmjerena na istraživanja, razvoj i komercijalizaciju termoenergetskih izvora nove generacije loženih fosilnim gorivom ukupne električne snage od 40 000 MW.

Smatra se da bi do 2030. troškovi HITS-a trebali biti smanjeni na 25 USD/t CO₂ do 50 USD/t CO₂ i postati ekonomski atraktivni, to jest biti niži od cijena jedne emisijske dozvole koja se mora osigurati za pogon termoelektrane bez HITS-a

Hvatanje CO₂ je dominirajuće u ukupnom trošku. Ukoliko se uzme u račun buduća povećana efikasnost, trošak hvatanja može biti smanjen sa sadašnjih procijenjenih od 50 USD/t CO₂ na oko 10 USD/t CO₂ do 25 USD/t CO₂ za loženje ugljenom i do 25 USD/t CO₂ do 30 USD/t CO₂ za plinom ložene termoenergetske proizvodne jedinice.

Troškovi transporta CO₂ po toni više ovise o volumenu koji se transportira, a manje od udaljenosti. Za cijevni transport količina većih od 1 000 kt CO₂ godišnje na udaljenosti veće od 500 km procjenjuju se troškovi transporta u rasponu od 1 USD/t CO₂ do 10 USD/t CO₂. Injektiranje CO₂ se procjenjuje na 2 USD/t CO₂ i to za količinu od 1 000 kt u slane vodonosnike, te do 50 USD/t CO₂ ECBM projekte.

8 CITS COSTS

There are no reliable estimates of total CITS costs as well as of particular costs of the technological chain. Most technologies have not been tested on demonstration plants of large unit capacities – their satisfactory operation has only been shown on pilot plants (Table 5).

The European Union has set up a system of trade in greenhouse gas emission units (EU-ETS), within which allowed emission levels for industries are determined and the system of trade in emission permits is set up. The price of emission permit on the market amounted to about 15 EUR/t in December 2008. With this price of emission permits, it is not cost-effective to activate CITS construction projects because they are not economically self-sustainable. At the moment, it is possible to estimate very roughly, due to a high number of options, that the total cost of the CITS technology would be between 50 USD/t CO₂ and 100 USD/t CO₂ of reduced emission. Until economic self-sustainability of the CITS is achieved, financial incentives will be necessary. Before the global economy crisis began, at the end of 2008, the European Union had a draft proposal of the energy investment plan at the amount of 200 billion euros until 2030. Along with impacting other trade mechanisms, it would be focused on research, development and commercialization of thermal energy sources of the new generation fired by fossil fuels of total power of 40 000 MW (electric).

It is believed that by 2030, CITS costs should fall to between 25 USD/t CO₂ and 50 USD/t CO₂ and become economically attractive, that is, become lower than the prices of an emission permit which is to be ensured for the operation of a thermal power plant without the CITS.

CO₂ capture is dominant item in the total cost. If the future increased efficiency is taken into account, the capture cost can fall from the today's estimate of 50 USD/t CO₂ to about 10 USD/t CO₂ up to 25 USD/t CO₂ for coal-firing and to 25 USD/t CO₂ up to 30 USD/t CO₂ for gas-fired thermal power production units.

CO₂ transportation costs per ton depend more on the volume of the transport and less on the distance. For pipeline transport of annual amounts larger than 1 000 kt CO₂ to distances higher than 500 km transportation costs are estimated in the range between 1 USD/t CO₂ and 10 USD/t CO₂. CO₂ injection is estimated at 2 USD/t CO₂ and that for the quantity of 1 000 kt in saline aquifer, and up to 50 USD/t CO₂ for ECBM projects.

Part of the CITS costs can be covered by income from increased fossil fuels extract efficiency. In certain specific projects, income could reach as

Dio troškova HITS može biti pokriven prihodima od povećane efikasnosti vađenja (iscrpk) fosilnih goriva. U nekim specifičnim projektima mogu prihodi dosegnuti i do 50 USD/t CO₂. Za neke od pripremljenih tehnologija HITS-a procjenjuje se da bi troškovi proizvodnje električne energije trebali biti povećani za 1 US\$/kWh do 2 US\$/kWh.

Članice EU su postavile sljedeće istraživačko razvojne prioritete:

- hvatanje CO₂ i proizvodnja vodika iz plinovitih fosilnih goriva,
- nadziranje i verificiranje geoloških spremnika,
- priprema masovne proizvodnje vodika iz dekarboniziranih fosilnih goriva uključujući i geološke spremnike,
- napredne tehnike hvatanja i izdvajanja,
- obilježavanje i karakterizacija potencijalnih geoloških spremnika, usklađivanje izvora i ponora,
- koordinacija i izrada mrežnih planova aktivnosti za HITS.

Predloženo je, 2008. godine, od parlamentarne grupe EU Parlamenta da za nove termoelektre, kapaciteta većeg od 300 MW, nakon 2015. godine najveća dozvoljena prosječna godišnja emisija CO₂ bude 500 g/kWh. To znači da bi bilo dozvoljeno graditi bez HITS samo termoelektre ložene prirodnim plinom jer je na današnjem razvoju tehnike tipična emisija za loženje ugljena između 700 g/kWh i 850 g/kWh, a za tekuće gorivo 590 g/kWh.

much as 50 USD/t CO₂. For some of the prepared CITS technologies, the increase of electricity production costs is estimated at 1 US\$/kWh up to 2 US\$/kWh.

EU member states have established the following research and development priorities:

- CO₂ capture and production of hydrogen from gaseous fossil fuels,
- supervision and verification of geological reservoirs,
- preparation of mass production of hydrogen from decarbonised fossil fuels including geological reservoirs,
- advanced capture and isolation technologies,
- marking and characterization of potential geological reservoirs, harmonization of sources and sinks,
- coordination and elaboration of network plans for the CITS activities.

In 2008, a EU Parliament group suggested that for new thermal power plants with a capacity of more than 300 MW, after the year 2015, the maximum allowed average annual CO₂ emission should be 500 g/kWh. That means that it would be allowed to construct, without CITS, only thermal power plants fired by natural gas because at today's level of technical development, the typical emission at coal firing is between 700 g/kWh and 850 g/kWh, and for liquid fuels it is 590 g/kWh.

Tablica 5 – Pregled trenutačne tržišne zrelosti sastavnica sustava HITS-a [4]
Table 5 – Overview of the current market maturity of the CITS system components [4]

HITS sastavnica / CITS component	Tehnologija / Technology	Razvoj / Development	Demonstracijska faza / Demonstration phase	Uvjetno ekonomski opravdano / Conditionally economically justified	Na tržištu provjeren / Market-tested
Hvatanje / Capture	Nakon izgaranja / Post-combustion			X	
	Prije izgaranja / Pre-combustion			X	
	Izgaranje u struji kisika / Oxyfuel		X		
	Industrijske separacije (procesiranje prirodnog plina, proizvodnja amonijaka) / Industrial separations (processing natural gas, ammonium production)				X
Transport / Transport	Cjevovodima / By pipelines				X
	Brodovima / By ships			X	
Podzemno spremanje / Underground storage	Povećanje iscrpka nafte utiskivanjem / Enhanced oil recovery by injection			X	X
	Povećanja iscrpka plina utiskivanjem / Enhanced gas recovery by injection			X	
	Otplinjavanje (metana) ležišta ugljena / Coal bed (methane) degassing		X		
	Iskorištena naftna ili plinska polja / Depleted oil or gas fields			X	
Spremanje u oceane / Storage in oceans	slani vodonosnik / saline aquifer			X	
	Direktno injektiranje – otopina / Direct injection – solution	X			
Mineralizacija / Mineralization	Direktno injektiranje – tekuće stanje / Direct injection – liquid state	X			
	Silikati / Silicates	X			
Industrijska namjena / Industrial use	Kruti otpad / Crude waste		X		X

Napomena: EOR je tržišno konkurentna tehnologija za povećanje iscrpka, ali i uvjetno opravdana ukoliko bude korištena primarno za spremanje CO₂
Remark: The EOR is a market-competitive technology for enhanced recovery but it is also conditionally justified if it is used for primary storage of CO₂.

9 ZAKLJUČAK

Izgaranje ugljena je odgovorno za 71 % emisije CO₂, prirodni plin za 18 % a loživo ulje za 11 % [12]. Povijesno gledano ljudska civilizacija je izgaranjem fosilnih goriva od 1751. do 2002. godine dostigla zbirnu emisiju u Zemljinu atmosferu od oko 1 000 Gt CO₂, dok će u idućih 28 godina prema nekim projekcijama [3], ukoliko ne dođe do promjene globalne energetske politike emitirati još 750 Gt CO₂ (!). Očito je da su potrebna veoma velika financijska ulaganja u razvoj novih projekata i poticanje paralelnih industrijskih i akademskih inicijativa te što veći broj tehničkih demonstracija tehnologija čija je vjerojatnost primjene izgledna na postrojenjima industrijskih razmjera.

Velika očekivanja se polažu u dobre rezultate pogona, do 2020. godine, HITS postrojenja koja će biti implementirana u novim termoenergetskim i kemijskim kompleksima u Alžiru (Salah), Velikoj Britaniji (Peterhead), USA-u (Carson), Australiji (Kwinana) i Norveškoj (Sleipner) [13]. U njima će rasplinjavanjem prirodnog plina biti proizvedena električna energija, vodik za dalje korištenje u energetici i transportu, a uhvaćeni, izdvojeni i transportirani ugljikov dioksid će biti spremljen u bušotine plina u neposrednoj blizini.

Za čisti ugljen bez emisije ugljikovog dioksida trebalo bi nešto duže vremena, jer je nužno ubrzati razvoj novih materijala koji bi trebali izdržati dugogodišnja toplinska naprezanja na visokim temperaturama pregrijane pare od 700 °C i postići neto učinak postrojenja iznad 50 % u trajnom pogonu.

Globalni problem, na koji danas nema zadovoljavajućih odgovora, bit će transport i nadzor skladišta ugljikovog dioksida velikih razmjera i to do oko 10 Gt CO₂ godišnje. Uočena propuštanja, često s velikim vremenskim kašnjenjem, neće moći biti otklonjena promptno, već u dužem periodu ili nikada. Zbog toga je nužno snažno politički podržati i financirati napore u razvoju, istraživanju i primjeni novih tehnoloških koncepcija i izbjeći, ili bar usporiti, katastrofalne posljedice klimatskih promjena koje se uočavaju zadnjih desetljeća.

9 CONCLUSION

Coal combustion accounts for 71 % of CO₂ emission, natural gas for 18 % and heating oil for 11 % [12]. Viewed historically, by combustion of fossil fuels from 1751 to 2002, human civilization has reached an aggregate emission into the Earth's atmosphere of about 1 000 Gt CO₂, while in the next 28 years, according to some predictions [3], if no change occurs as regards the global energy policy, another 750 Gt CO₂ will be emitted (!). It is obvious that very extensive financial investments in the development of new projects and the stimulation of parallel industrial and academic initiatives are necessary, as well as a large number of technical demonstrations of the technologies the application of which will probably take place on plants of industrial dimensions.

The operations of the CITS plants that will be implemented in the new thermal power plants and chemical complexes in Algiers (Salah), Great Britain (Peterhead), USA (Carson), Australia (Kwinana) and Norway (Sleipner) [13] are expected to yield good results by 2020. There, by natural gas combustion, electricity will be produced, as well as hydrogen for further use in the energy/transport sector, and the captured, isolated and transported carbon dioxide will be stored into gas boreholes in the direct vicinity.

The obtainment of pure coal without carbon dioxide emission will take some more time because it is necessary to speed up the development of new materials which should endure years of thermal stress at high overheated vapour temperatures of 700 °C and achieve net plant output higher than 50 % in permanent operation.

The global problem, which cannot be answered today, will be the transport and supervision of carbon dioxide reservoirs of large dimensions and that being as much as 10 Gt CO₂ annually. It will be impossible to promptly remove the leakages observed, often with a delay in time, but in a longer period of time or never. It is therefore necessary for the policies to support adamantly and finance the efforts of the development, research and application of new technological concepts and to avoid, or at least slow down, catastrophic consequences of climatic changes which have been observed in the last decades.

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