

**Małgorzata Formela*, Stanisław Stryczek*,
Rafał Wiśniowski*, Anna Pikłowska***

SELECTING RECIPES OF CEMENT SLURRY FOR SEALING CASING COLUMNS IN WELLBORES USED FOR CCS**

1. INTRODUCTION

One of the most important environmental issues bothering scientists nowadays are greenhouse gases, mainly carbon dioxide, and the possibility of limiting their emission and utilization the already ones. Many countries have been active trying to limit the greenhouse gases emission, mainly carbon dioxide, and implement Carbon Capture and Storage (CCS) technology for years.

Carbon dioxide can be sequestered with the following methods [13]:

- physical (e.g. geological deposition),
- chemical (e.g. mineral carbonation),
- biological (e.g. growing forests).

Geological deposition of CO₂ as part of the Carbon Capture and Storage (CCS) technology can be realized through (Fig. 1):

- deposition in deep salt aquifers (they have the highest potential and still remain useless for other purposes),
- deposition in depleted beds of hydrocarbons (potentially with Enhanced Oil Recovery (EOR), or enhanced natural gas recovery),
- deposition in deep coal beds (not extracted) with Enhanced Coal Bed Methane Recovery (ECBMR) [13, 14].

One of the most important aspects of geological deposition is providing environmental safety. The safety of CO₂ deposition must be taken into account at the planning and realization stage. All possibilities of carbon dioxide leaks occurrence should be accounted for. The safety of CO₂ storing mainly depends on the geological structure of rocks, in which the gas

* AGH University of Science and Technology, Faculty of Drilling, Oil and Gas, Krakow, Poland

** Work realized at the Department of Drilling and Geoengineering, Faculty of Drilling, Oil and Gas AGH-UST within the Statutory Research Program No. 11.11.190.555 WP2

is deposited, physical and chemical processes taking place there and also infrastructure. The wells through which CO₂ is injected and the closed objects are the most probable pathways through which gas may escape, especially when the hardened sealing slurry corrodes.

CO₂ leaks may take place through the injection well or along its length after CO₂ has been already injected. This problem refers to all types of geological storing [10–12].

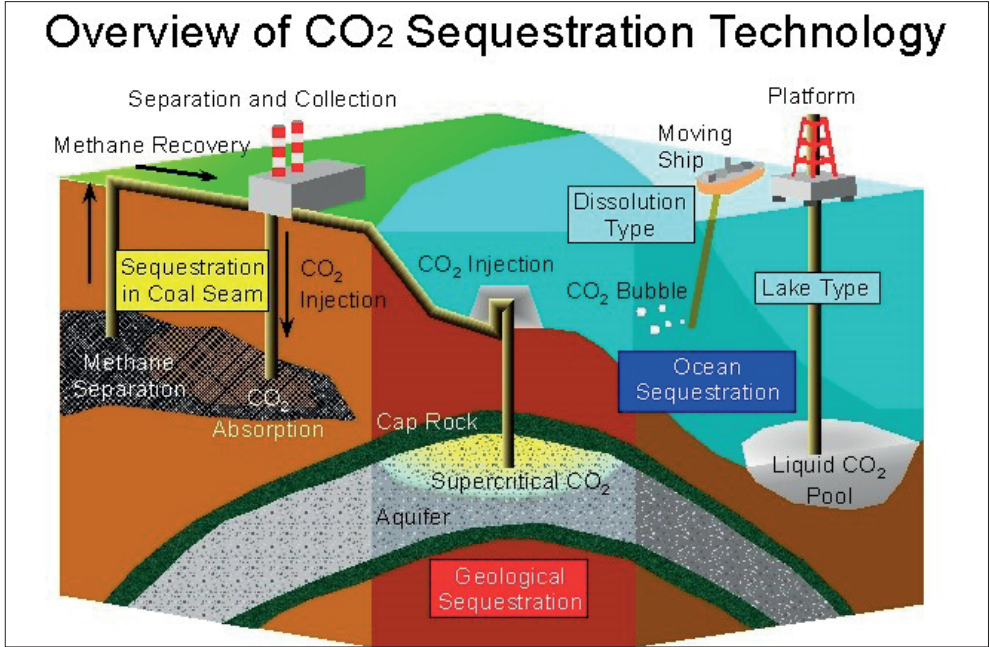


Fig. 1. CCS potential [14]

In the case of storing in depleted oil or gas deposits, problems appear not only in reference to the CO₂ injection wells but also liquidated wells and closed with cement plugs. Thus it is very important to properly select cement at the stage of designing and performing wells designed for CO₂ injection and liquidation. The leaks through the corroded cement slurry are considered to be a huge environmental hazard [10, 11].

The leaks through the damaged hardened cement stone to the rock mass are mostly caused by carbonate corrosion caused by the presence of aggressive CO₂ in water or air. Calcium ions are leached out of cement, first from Ca(OH)₂, constituting one of the products of hydration of basic components of Portland cement (alite and belite), then also hydrated silicate (C-S-H) and hydrated calcium aluminate [3].

The risk connected with geological deposition of carbon dioxide is one of the biggest issues having impact on the social acceptance of the CCS technology. The cement slurry should be appropriately selected and the role of CO₂ in the development of technological properties of fresh and hardened cement slurry determined. Obviously the negative impact of CO₂ on the properties of fresh and hardened cement slurry may disturb the exploitation of the well and create considerable hazard for the geological storage of carbon dioxide [10–12].

2. CARBONATE CORROSION

In the case of geological deposition of carbon dioxide it is carbonate corrosion or acid-carbonate corrosion which threatens cement slurry. First the cement hydration products are carbonized, then calcium ions leached out of cement slurry, first from $\text{Ca}(\text{OH})_2$, and gradually as it is washed out, also from hydrated silica, hydrated calcium aluminate and hydrated calcium sulfate-aluminate [1, 3, 4].

The durability of cement slurries is also affected by:

- the mineralization of reservoir waters,
- the presence of brines,
- high temperature.

All products of cement hydration undergo carbonation.

At the first stage of the carbonation, gaseous CO_2 is dissolved in water and $\text{CO}_2(\text{aq})$ is formed. Then H_2CO_3 is formed to dissociate to H^+ , HCO_3^- , CO_3^{2-}

When CO_2 – saturated water diffuses to the cement slurry matrix, $\text{Ca}(\text{OH})_2$ is dissolved in a carbonic acid solution. Dissolving of portlandite is connected with the migration of Ca^{2+} ions to the solution, as a consequence of which of CaCO_3 is formed [3, 4].

At the initial stage of carbonation cement slurry is sealed under the influence of the hardly soluble CaCO_3 . The solution in the pores of the slurry (pore fluid) is strongly alkaline, with pH equal to about 13. When pH of the pore fluid lowers as a result of carbonization to about 10.5, the CO_3^{2-} ions dominate and CaCO_3 is stable and durable. At that time the slurry has lower permeability, which results from the fact that part of the pores are blocked with the formed CaCO_3 . The strength of the hardened cement slurry increases. When portlandite and alkaline phases are depleted in the cement slurry matrix, the pH of the solution lowers and HCO_3^- start to dominate in the solution. Then, CaCO_3 dissolves as a result of which Ca^{2+} ions are washed out from the cement matrix, and CaCO_3 assumes the form of w calcium hydrogen carbonate. Hardened slurry, devoid of CaCO_3 , cannot buffer pH, as a consequence of which the hydrated calcium silicate C-S-H loses Ca^{2+} and takes the form of amorphous silica gel.

The formation of amorphous silica gel increases porosity, lack of coherence (continuity) of microstructure of cement slurry, and so lower strength in longer time intervals.

The basic carbonization product is calcium carbonate, which is present in the cement slurry in various phases. Vaterite is probably formed first, then it takes the form of calcite with aragonite as a transition state [3, 4].

The problem of durability of slurries which are to be used for cementing casing columns in wellbores for CO_2 storing is complex therefore all aspects should be analyzed and the employed research methods so selected as to guarantee working out a recipe which would have the required resistance and durability in the existing wellbore conditions [12].

Hardened cement slurry used in wellbores for carbon dioxide storing should have lower fluids and gases permeability [11, 12]. One of the most important factors having an effect on the permeability coefficient is the water to cement ratio (w/c), which decides about the capillary porosity. Capillary pores generate the flow of aggressive solutions inside the hardened slurry, which may lead to reactions accelerating chemical corrosion. Each change of cement slurry pH may cause faster or slower decomposition of hydrates. This means that

acidic solutions (mainly acids) of low pH (ca. 5) will make the hardened slurry dissolve. Among the most reactive compounds which quickly react with the slurry hydration products are sulfates and chlorides [1, 4]. Water film gathering on the mineral filler grains increases the porosity on the slurry/filler interface, where many calcium hydroxide particles are present. This leads to the local increase of w/c ratio. This process can be stopped by applying a mineral additive to the slurry, i.e. silica powder containing about 98% SiO₂. Silica powder reacts with calcium hydroxide forming C-S-H phase, which increases the durability of hardened slurry in a corrosive environment [1, 3].

The effect of adding silica powder on hydration processes is illustrated in Figure 2.

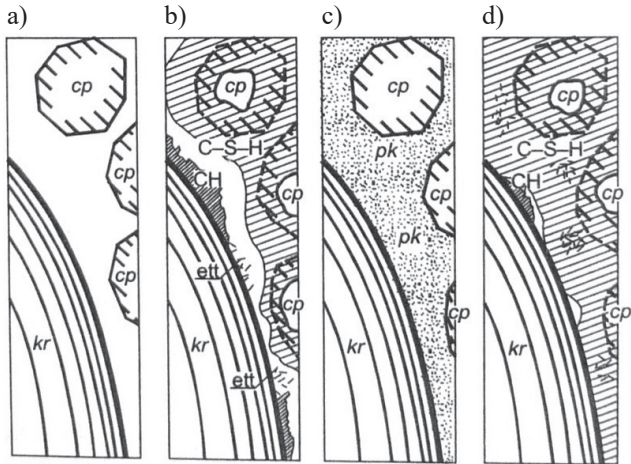


Fig. 2. Influence of silica powder on the build of the slurry/aggregate interface: cp – cement grains; pk – silica powder; a)–d) progress of hydration [4]

The destruction of hardened slurry may stem from single or concurrent processes favoring corrosion.

Carbonization has an effect on the pore structure in the slurry. Total porosity is lowered and the distribution of pores is shifted to higher values.

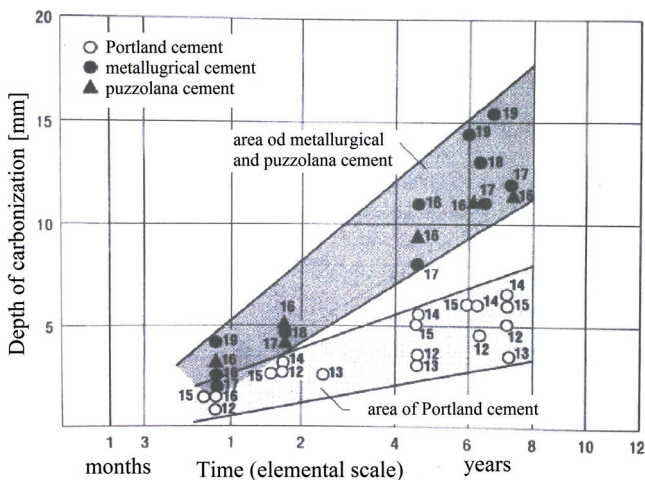
The carbonization process is described with the formula:

$$x = a\sqrt{t} \tag{1}$$

where:

- x – thickness of carbonized layer,
- a – constant,
- t – time.

Corrosion develops faster in cements containing over 30% of fly ashes and 50% more slag. The influence of the cement type on the depth of carbonization of the slurry is presented in Figure 3 [3].



The results of compressive and flexural tests of hardened cement slurries placed in network water and CO₂ have been presented in Table 1. The time of deposition of samples in a given environment equaled to 1, 2, 7, 14, 28, 90, 180 and 270 days [1, 5].

Table 1
Flexural and compressive strength of cement stone at temperature 20 (±2°C) [1]

Composition of sample		Drilling cement G (API) + 40% fluidal ash + 0% SPL		Drilling cement G (API) + 40% fluidal ash + 1.40% SPL		Drilling cement G (API) + 40% fluidal ash + 2.0% SPL	
		Environment					
Number of days after which sample was tested		water	CO ₂	water	CO ₂	water	CO ₂
		Flexural strength [MPa]	1	9,231	–	9,422	–
2	10,391		–	10,493	–	9,818	–
7	12,618		–	13,787	–	12,975	–
14	13,668		12,04	13,855	14,297	12,844	13,893
28	13,528		14,701	12,559	16,201	14,327	17,043
90	10,736		10,383	10,349	10,935	10,468	11,326
180	5,002		10,119	5,627	10,072	11,862	11,785
270	3,5		11,335	4,1	9,707	10,162	10,77
Compressive strength [MPa]	1	23,958	–	21,563	–	23,646	–
	2	30,521	–	29,479	–	31,354	–
	7	30	–	30,938	–	31,458	–
	14	30,208	36,042	33,333	42,917	33,75	35,833
	28	38,854	36,042	29,063	31,25	30,417	33,333
	90	48,638	34,479	51,937	39,583	51,183	38,646
	180	50,254	36,042	55,153	39,896	42,292	36,563
	270	43,9	48,362	52,7	43,845	48,365	50,228

The analysis of the results of mechanical strength tests reveals that the recipes of slurries containing 2% superplasticizer have the highest values of all analyzed recipes. Accordingly, this particular recipe has been SEM analyzed for phase composition at the Faculty of Materials Science and Ceramics.

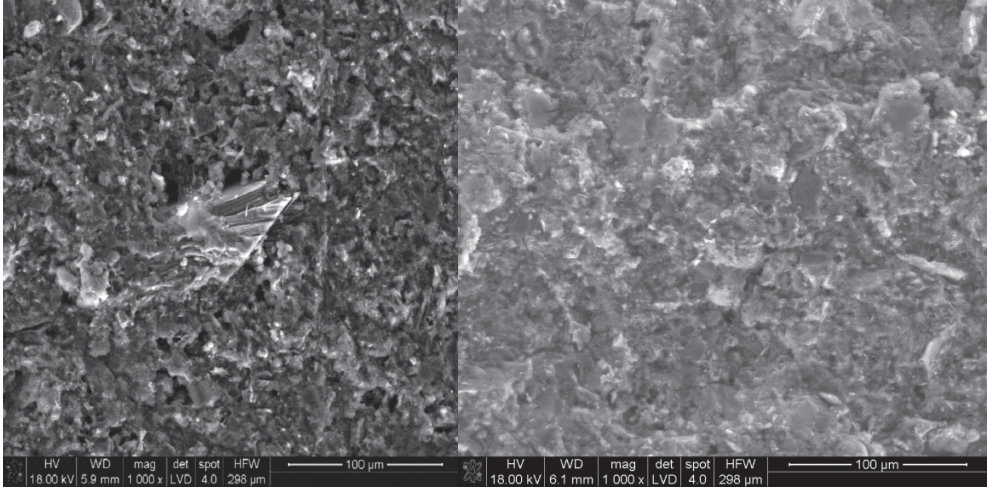


Fig. 4. Microstructure of cement slurry after 28 days (left: water, right: CO₂) [1]

The first sample (Fig. 4) was observed to have partly clustered fibrous C-S-H. A black fibrous break was noted in the sample. The visible portlandite flakes prove an advanced state of hydration of the sample.

In the second sample authors observed a small number of hydroxide crystals and the presence of luminoferrite. Analogous to the first sample, C-S-H was present in the pores.

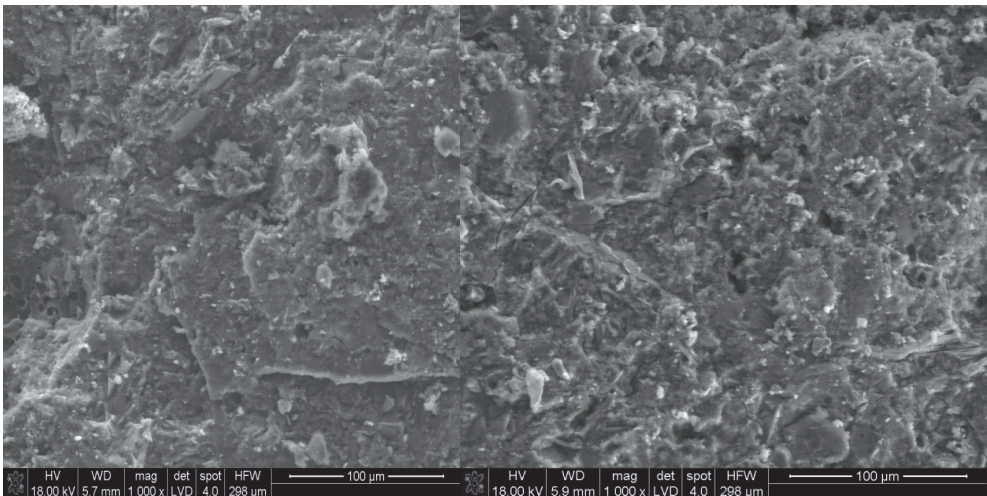


Fig. 5. Microstructure of cement slurry after 90 days (left: water, right: CO₂) [1]

In Figure 5 we can see a small change in the mineral composition in a sample placed in an aqueous environment and a sample disposed in CO_2 . In the first one $30\ \mu\text{m}$ crystals of calcium hydroxide are visible. They usually originate the CO_2 -induced corrosion. The remaining part of the sample consists of C-S-H phase and small pores.

In the second sample, which was exposed to an aggressive environment, no negative activities relating to the presence of carbon dioxide were observed in the structure.

The analysis of the microstructure (Fig. 6) of a sample placed in an aqueous environment (left) revealed that it was highly porous which may indicate that it was saturated in the process of its preparation. It has a consolidated build. No big amounts of calcium aluminate have been observed in it.

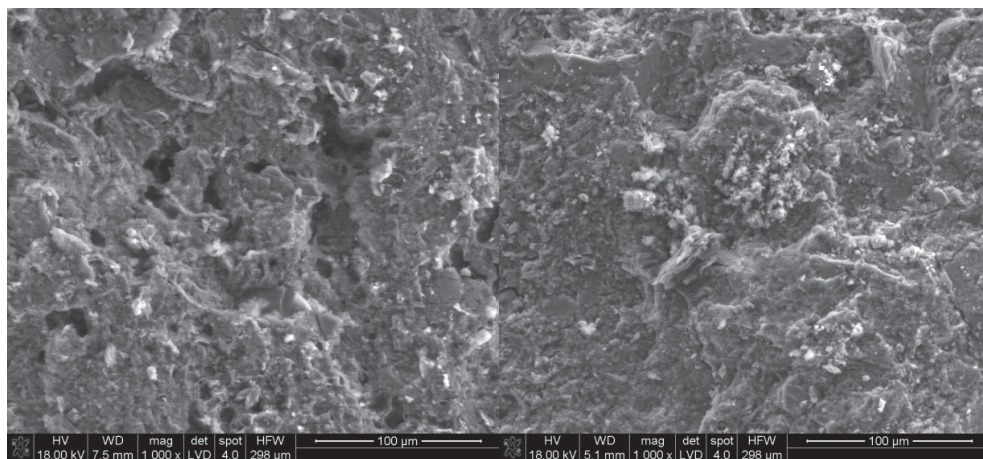


Fig. 6. Microstructure of cement slurry after 270 days (left: water, right: CO_2) [1]

The other sample illustrates the carbonization process. It manifests itself mainly in the form of small balls and pills of surface. Fine crystalline aggregates of calcium carbonate, responsible for this process, are present in the pores.

4. CONCLUSIONS

The following general conclusions can be drawn on the basis of the results of the conducted research:

1. A negative effect of an aggressive environment on cement slurry, i.e. carbon dioxide, requires extensive studies of its impact on the technological parameters of fresh and hardened sealing slurry.
2. In wells where there exists the risk of carbon dioxide presence, special attention should be paid to inorganic mineral additives, highly resistant to the corrosiveness of CO_2 .
3. The addition of fluidal ash from the combustion of lignite influences the economics and the technological process for wells which can be used for CCS.

4. The increased concentration of the superplasticizer in the cement slurry where fluidal ash was added, considerably changed its rheological properties.
5. Different concentrations of superplasticizer GLENIUM® SKY 591 significantly change the rheological properties of fresh slurries and the strength of hardened cement slurry.
6. The microscopic analysis of the selected sample reveals that the presence of carbon dioxide does not lower the compressive and flexural strength of the slurry; what is more it considerably increases these parameters.
7. The analyses and final results show that the addition of fluidal ash from the combustion of lignite and different concentration of superplasticizer GLENIUM® SKY 591 favorably affects the properties of slurries. The use of both of these additives results in lowering of the cost and a more environmentally friendly aspect.

REFERENCES

- [1] Formela M.: *Wpływ dwutlenku węgla na parametry świeżego i stwardniałego zaczynu cementowego*. Kraków 2014 [unpublished].
- [2] Giergiczny Z.: *Popiół lotny w składzie cement i betonu*. Wydawnictwo Politechniki Śląskiej, Gliwice 2013.
- [3] Kurdowski W.: *Chemia cementu i betonu*. Wydawnictwo Polski Cement –Wydawnictwo Naukowe PWN, Kraków 2010.
- [4] Kurdowski W.: *Chemia materiałów budowlanych*. Uczelniane Wydawnictwo Naukowo-Dydaktyczne AGH, Kraków 2003.
- [5] PN-EN 450-1: 2012. *Popiół lotny do betonu. Część 1: Definicje, specyfikacje i kryteria zgodności*.
- [6] PN-EN 934-1: 2009. *Domieszki do betonu, zapraw i zaczynu*.
- [7] Stryczek S., Brylicki W., Małolepszy J., Gonet A., Wiśniowski R., Kotwica Ł.: *Influence of fly ash formed in brown coal fluidal combustion process on the properties of pastes incorporating large amount of blast-furnace slag*. Ninth CANMET/ACI international conference on the use of fly ash, slag, silica fume and other supplementary cementing materials in concrete technology, Warsaw, Poland, May 20–25, 2007.
- [8] Stryczek S., Małolepszy J., Gonet A., Wiśniowski R., Kotwica Ł.: *Wpływ dodatków mineralnych na kształtowanie się właściwości technologicznych zaczynów uszczelniających stosowanych w wiertnictwie i geoinżynierii*. Wydawnictwo S.C.M.R., Kraków 2011.
- [9] Stryczek S., Małolepszy J., Gonet A., Wiśniowski R., Kotwica Ł., Złotkowski A., Ziaja J.: *Popioły z fluidalnego spalania węgla brunatnego jako dodatek do zaczynów uszczelniających*, red. S. Stryczek. Wydawnictwa AGH, Kraków 2013.
- [10] Tarkowski R.: *Geologiczna sekwestracja CO₂*. Studia, Rozprawy, Monografie, nr 132, Instytut Gospodarki Surowcami Mineralnymi i Energią Polskiej Akademii Nauk, Kraków 2005.
- [11] Uliasz-Bocheńczyk A.: *Składowanie CO₂ z zawiesinami popiołowo-wodnymi pod ziemią*. Instytut Gospodarki Surowcami Mineralnymi i Energią Polskiej Akademii Nauk, Kraków 2007.

- [12] Uliasz-Bocheńczyk A.: *Zaczyny cementowe w technologiach wiertniczych geologicznego składowania CO₂*. Studia, Rozprawy, Monografie, nr 176, Instytut Gospodarki Surowcami Mineralnymi i Energią Polskiej Akademii Nauk, Kraków 2012.
- [13] Uliasz-Bocheńczyk A., Mokrzycki E., *Przegląd możliwości utylizacji ditlenku węgla*. Wiertnictwo, Nafta, Gaz, nr 22, 2005, pp. 373–378.
- [14] <http://www.rite.or.jp/English/welcome/Project/sequestration/sequestration.html> [06.06.2016].