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Historical Review

More than 90 years have passed since the University Ljubljana in Slovenia was founded in 1919. Technical fields were united in the School of Engineering that included the Geologic and Mining Division, while the Metallurgy Division was established only in 1939. Today, the Departments of Geology, Mining and Geotechnology, Materials and Metallurgy are all part of the Faculty of Natural Sciences and Engineering, University of Ljubljana.

Before World War II, the members of the Mining Section together with the Association of Yugoslav Mining and Metallurgy Engineers began to publish the summaries of their research and studies in their technical periodical Rudarski zbornik (Mining Proceedings). Three volumes of Rudarski zbornik (1937, 1938 and 1939) were published. The War interrupted the publication and it was not until 1952 that the first issue of the new journal Rudarsko-metalurški zbornik - RMZ (Mining and Metallurgy Quarterly) was published by the Division of Mining and Metallurgy, University of Ljubljana. Today, the journal is regularly published quarterly. RMZ - M&G is co-issued and co-financed by the Faculty of Natural Sciences and Engineering Ljubljana, the Institute for Mining, Geotechnology and Environment Ljubljana, and the Velenje Coal Mine. In addition, it is partly funded by the Ministry of Education, Science and Sport of Slovenia.

During the meeting of the Advisory and the Editorial Board on May 22, 1998, Rudarsko-metalurški zbornik was renamed into "RMZ – Materials and Geoenvironment (RMZ – Materiali in Geookolje)" or shortly RMZ – M&G. RMZ – M&G is managed by an advisory and international editorial board and is exchanged with other world-known periodicals. All the papers submitted to the RMZ – M&G undergoes the course of the peer-review process.

RMZ – M&G is the only scientific and professional periodical in Slovenia which has been published in the same form for 60 years. It incorporates the scientific and professional topics on geology, mining, geotechnology, materials and metallurgy. In the year 2013, the Editorial Board decided to modernize the journal's format.

A wide range of topics on geosciences are welcome to be published in the RMZ – Materials and Geoenvironment. Research results in geology, hydrogeology, mining, geotechnology, materials, metallurgy, natural and anthropogenic pollution of environment, biogeochemistry are the proposed fields of work which the journal will handle.

Zgodovinski pregled

Že več kot 90 let je minilo od ustanovitve Univerze v Ljubljani leta 1919. Tehnične stroke so se združile v Tehniški visoki šoli, ki sta jo sestavljala oddelka za geologijo in rudarstvo, medtem ko je bil oddelek za metalurgijo ustanovljen leta 1939. Danes oddelki za geologijo, rudarstvo in geotehnologijo ter materiale in metalurgijo delujejo v sklopu Naravoslovnotehniške fakultete Univerze v Ljubljani.

Pred 2. svetovno vojno so člani rudarske sekcije skupaj z Združenjem jugoslovanskih inženirjev rudarstva in metalurgije začeli izdajanje povzetkov njihovega raziskovalnega dela v Rudarskem zborniku. Izšli so trije letniki zbornika (1937, 1938 in 1939). Vojna je prekinila izdajanje zbornika vse do leta 1952, ko je izšel prvi letnik nove revije Rudarsko-metalurški zbornik – RMZ v izdaji odsekov za rudarstvo in metalurgijo Univerze v Ljubljani. Danes revija izhaja štirikrat letno. RMZ – M&G izdajajo in financirajo Naravoslovnotehniška fakulteta v Ljubljani, Inštitut za rudarstvo, geotehnologijo in okolje ter Premogovnik Velenje. Prav tako izdajo revije financira Ministrstvo za izobraževanje, znanost in šport.

Na seji izdajateljskega sveta in uredniškega odbora je bilo 22. maja 1998 sklenjeno, da se Rudarsko-metalurški zbornik preimenuje v RMZ – Materiali in geookolje (RMZ – Materials and Geoenvironment) ali skrajšano RMZ – M&G. Revijo RMZ – M&G upravljata izdajateljski svet in mednarodni uredniški odbor. Revija je vključena v mednarodno izmenjavo svetovno znanih publikacij. Vsi članki so podvrženi recenzijskemu postopku.

RMZ – M&G je edina strokovno-znanstvena revija v Sloveniji, ki izhaja v nespremenjeni obliki že 60 let. Združuje področja geologije, rudarstva, geotehnologije, materialov in metalurgije. Uredniški odbor je leta 2013 sklenil, da posodobi obliko revije.

Za objavo v reviji RMZ – Materiali in geookolje so dobrodošli tudi prispevki s širokega področja geoznanosti, kot so: geologija, hidrologija, rudarstvo, geotehnologija, materiali, metalurgija, onesnaževanje okolja in biokemija.

Glavni urednik

Editor-in-Chief

Interaction between Al 99.5 and stainless steel at elevated temperature and pressure

Interakcija med Al 99,5 in nerjavnim jeklom pri povišani temperaturi in tlaku

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Abstract

The aim of this work was to investigate interaction between aluminium 99.5 and austenitic stainless steel 1.4301 or ferritic stainless steel 1.4767 at elevated temperature and pressure. Three series of tests were done. Samples were pressed with Thermomechanical simulator of metallurgical states "Gleeble 1500D". Before each series of bonding, aluminium 99.5 was cleaned in a liquid agent for degreasing and removal of oxides "Nabadur 152 (5 %)". After pressing, the samples were prepared for metallographic analysis. Samples were analyzed under an optical or a scanning electron microscope.

Cleaning agent Nabadur 152 (5 %) ensures proper cleanliness of the surface of the aluminium, the steel is not needed to be cleaned. The formation of the joint is heavily dependent on the geometry of the tool. In order to achieve a good bond, bonding at a temperature of 550 °C or more is required. The holding time at the temperature for successful bonding should be at least 5 s. Minimum force required for the formation of the bond is 13 kN.

Key words: bonding, aluminium alloys, stainless steel, elevated temperature, elevated pressure

Izvleček

Namen dela je bil ugotoviti optimalne razmere za spajanje avstenitnega nerjavnega jekla 1.4301 oziroma feritnega nerjavnega jekla 1.4767 z aluminijem 99,5 pri povišani temperaturi in tlaku. Narejene so bile 3 serije preizkusov. Vzorce smo spajali s simulatorjem termomehanskih metalurških stanj Gleeble 1500D. Pred vsako serijo spajanja je bil aluminij 99,5 očiščen v tekočem sredstvu za razmaščevanje in odstranjevanje oksidov Nabadur 152 (5 %). Po stiskanju so bili vzorci pripravljeni za metalografsko analizo. Vzorci so bili analizirani z optičnim oziroma vrstičnim elektronskim mikroskopom.

Čistilno sredstvo Nabadur 152 (5 %) zagotovi ustrezno čistočo površine aluminija, tako da jekla ni treba posebej čistiti. Nastanek spoja je močno odvisen od geometrije orodja. Za dosego spoja je potrebno spajanje pri temperaturi 550 °C ali več. Časi držanja na temperaturi spajanja morajo biti vsaj 5 s. Minimalna potrebna sila stiskanja za nastanek spoja je 13 kN.

Ključne besede: spajanje, aluminijeve zlitine, nerjavno jeklo, povišane temperature, povišan tlak

Introduction

Diffusion bonding of materials in the solid state is a process for making a monolithic joint with the formation of bonds at an atomic level as a result of joining the opposite surfaces due to local plastic deformation at elevated temperatures, which increases the interdiffusion at the surface layer of the materials, which are brought together.^[1]

Bonding in solid state is a joint mark for proceedings in which there is no bonding material, but the material is heated only to the pitting state and the bond is achieved by pressing. Here the surface is brought to the atomic level distance (distance between the atoms), therefore the adhesion forces influence on the bond. Due to the increase in temperature at the boundary layer the process of diffusion occurs. Because the bond is deformed due to the pressure, a combination with the high temperature processes of recrystallization occurs.^[2]

Prior to the joining of aluminium and stainless steel it is necessary to both materials are adequately prepared. It is very important that the surface is clean and of suitable roughness, because only in this way a good bond can be achieved. Stainless steel and aluminium have different melting temperature, so these materials must be bonded under the melting point of aluminium. Temperatures higher than 550 °C are problematic, because there is a softening of aluminium. For joining of steel and aluminium by rolling, the aluminium is heated up to a temperature of 450-550 °C, while the steel is heated to 400 °C. It is very important, that the oxides do not form on the surface, which would prevent the bonding. Problems at the bonding with the rolling process may be mainly caused by oxides in the steel, which are not disrupted, while the oxides of the aluminium may be disturbed easily.^[3] During the bonding brittle intermetallic phase may also be formed, which weakens the joint.^[4] The formation of this phase takes place at temperatures above 500 °C.^[5] The thickness of the intermetallic phase can be from a few nm to a few hundred µm. The most common phase resulting from the bond between the stainless steel and aluminium are phases from the ternary system Fe-Cr-Al. ^[6] To achieve the best possible bond,

it is important that the intermetallic phase is as narrow as possible or that they are not present. ^[4] Acceptable thickness of the intermetallic layer, which does not impact the strength of the bond is $3-5 \mu m$, while the thickness exceeding $10 \mu m$ causes the bond unusable. ^[7]

The bonding speed is also important, which vary from procedure to procedure. Speeds may range from a few cm/s and up to 1600 m/s at the explosion bonding. To achieve good joints between aluminium and steel at least 50 % deformation is required. The bonding time varies from a few hundredths of a second and up to several hours, and are dependent on the bonding process and other parameters, such as speed, temperature, pressure and atmosphere. The aim of this work was to investigate the interaction between aluminium 99.5 and austenitic stainless steel 1.4301 or ferritic stainless steel 1.4767 at elevated temperature and pressure.

The company Talum, d. d., wanted to produce new products which would be produced by bonding in the solid. The purpose of the study was to investigate the interaction between 99.5 aluminium and stainless steel, as well as to establish optimal conditions for achieving a good bond. To achieve a good bond it is very important the surface preparation, which has to be properly cleaned. All impurities must be removed, such as oxides, dust and moisture.

Experimental work

With the aim of bonding of aluminium 99.5 (AA1050, Table 1, soft annealed state) and austenitic stainless steel 1.4301 or ferritic stainless steel 1.4767 at elevated temperature and pressure, three different series of compression tests were made at various experimental conditions, presented in Table 2. Tests of bonding were carried out by Thermomechanical simulator of metallurgical states Gleeble 1500D. Bonding was carried out at different temperatures where the samples were induction heated to the testing temperature, holding at the coupling temperature times, the compression speeds and displacements of the tool on the sample surface of approximately 2 cm². Samples were subsequently analyzed by optical

(Olympus BX61) and scanning electron microscopy (Jeol 5610). Using a computer simulation program Thermo-Calc, based on different databases, a simulation of thermodynamic equilibrium bond formed between the steel and aluminium was produced.

In a first series 7 samples were compressed. Bonding was carried out at a temperature of 550 °C and 600 °C, movement of the tool was 0.4 mm, while the retention time at the temperature of compression was 0 s and 10 s. Samples 1.2, 1.5 and 1.6. were analysed using microscope. In the first two samples, a ferrite stainless steel 1.4767 and aluminium 99.5 were used, and in the third sample austenitic stainless steel 1.4301 was used. All three samples were compressed at a temperature of 550 °C, samples 1.5 and 1.6 were maintained at a temperature of compression for 10 s, while the sample 1.2 was only compressed. Formation of the bond was observed in samples 1.5 and 1.6, whereas at the sample 1.2 the bond was not achieved. At the samples where the bond was formed an intermediate layer was observed, whereas the thickness in the sample 1.5 was 4.08 μ m and in the sample 1.6 5.84 μ m. In both cases, the samples were compressed with a force of 13 kN. At the same time 59 % and 40.55 % deformation of aluminium was achieved.

In the second series 6 samples were compressed, using profiled tool. Bonding was carried out at a temperature of 560 °C. The displacement of the tool was set on 0.4 mm, tool speed was 100 mm/s, the holding times were (0, 2, 4, 6 and 8) s. From this series, the samples 2.1, 2.2, 2.3 and 2.4 were analyzed. In all samples aluminium 99.5 and ferritic stainless

 Table 1: Chemical composition of investigated Al-alloy Al99.5 (AA1050)

Alloy				Element					
AA1050	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
	0.07	0.26	< 0.001	-	< 0.001	-	< 0.002	< 0.007	99.50

Sample	Upper sample	Lower sample	Temperature (°C)	Movement (mm)	Holding time (s)
1.1	Al 99.5	1.4767	550	0.4	-
1.2	Al 99.5	1.4767	550	0.4	-
1.3	Al 99.5	1.4767	550	0.4	10
1.4	Al 99.5	1.4767	600	0.4	-
1.5	Al 99.5	1.4767	550	0.4	10
1.6	Al 99.5	1.4301	550	0.4	10
1.7	Al 99.5	1.4301	600	0.4	10
2.1	Al 99.5	1.4767	560	0.4	2
2.2	Al 99.5	1.4767	560	0.4	6
2.3	Al 99.5	1.4767	560	0.4	8
2.4	Al 99.5	1.4767	560	0.4	4
2.5	Al 99.5	1.4767	560	0.4	0
2.6	Al 99.5	1.4767	560	0.4	2
3.1	Al 99.5	1.4767	540	0.4	5
3.2	Al 99.5	1.4767	540	0.4	5
3.3	Al 99.5	1.4767	540	/	5
3.4	Al 99.5	1.4767	540	0.6	5
3.5	Al 99.5	1.4767	540	0.6	3
3.6	Al 99.5	1.4767	540	0.6	8

Table 2: Experimental samples

steel 1.4767 were used. At these conditions the bond in all sample was not achieved. In this series of compression test the compression force was ranging from 8 kN to 20.5 kN, while the deformation of the aluminium was in the range between 30 % and 60 %.

In the third series 6 samples were compressed (aluminium 99.5 and ferritic stainless steel 1.4767). Bonding was carried out with a profiled tool at a temperature of 540 °C. The displacement of the tool varied from 0.4 mm to 0.6 mm. The holding time at the temperature of compression (3 s, 5 s and 8 s) also varied. In this series, samples 3.3, 3.4 and 3.6 were thoroughly analyzed. Bond occurred only in the sample 3.6. In this sample, a force of 16 kN, and deformation of the aluminium 55.46 % were achieved. When the bond occurred, 1 μ m thick discontinuous intermediate layer appeared, whose composition corresponds to phases AlCr₂ and Al₈Cr.

Results and discussion

First series

Using optical microscopy samples 1.2, 1.5 and 1.6 were analyzed. The bond was achieved in samples 1.5 and 1.6. Therefore, in these two samples the analysis with a scanning electron microscope was made.

Sample 1.2 was heated up to 550 °C, where it was held for 5 s, so the temperature was constant over the entire sample. Then it was compressed with a force of 15 kN. The displacement was set to 0.4 mm. At the compression of the sample 1.2 there is a 43.2 % deformation of the aluminium, while no deformation of the steel occurred. The different width of the gap is due to non-parallel jaws and the tool during pressing.

Here, the sample 1.5 was heated to the temperature of 550 °C, pressed with a force of 13 kN, where it was held for 10 s. At this sample the bond occurred. Figure 1 shows the thickness of the individual areas of the sample 1.5 after compression. From the Figure 1 it can be seen that the bond formed along the entire length of the sample. In Figure 1a, which shows the left-compressed side of the sample, it can be seen that the thickness of the aluminium was 323.43 μ m and of the steel 475.50 μ m. On the right compressed side of the sample represented by the Figure 1b the thickness of the aluminium was 307.79 μ m, while the thickness of the steel was 470.35 μ m. Figure 1c shows a middle part of the compressed sample. Here the thickness of the aluminium was 311.84 μ m, the steel was 471.63 μ m. In the compressed part, where the bond was reached, the intermediate layer between the aluminium and steel is present, but it was not thick enough to be measured with an optical microscope. The thickness of the undeformed aluminium was 749.52 μ m and the thickness of the steel was 475.52 μ m (Figure 1d).

Figure 2 shows the three areas marked with numbers from 1 to 3, where the surface EDS analysis was made. The special attention was paid to the intermediate part of the bonded sample. From Figure 2 it can be seen that the area 1, the intermediate layer between the steel and aluminium, is composed from amount fractions 71.432 % Al, 4.842 % Cr and 23.726 % Fe. In the area 2, which presents the composition of the steel, is from 5.472 % Al, 0.271 % Si, 17.639 % Cr and 76.619 % Fe. Region 3, which presents the composition of aluminium, is composed from 99.833 % Al and 0.167 % Fe. In a sample 1.5 the thickness of the layer that is formed between aluminium and steel was also measured. The thickness of the intermediate layer was 4.08 µm and is shown in Figure 3.

Compressing test of the sample 1.6 took place at a temperature of 550 °C. Upon reaching the temperature of 550 °C, the sample was kept at the temperature for 5 s, in order to reach the constant temperature through the whole sample. Furthermore, the compressing of the sample took place with a force of 13 kN, and holding at a temperature of 550 °C for 10 s.

In Figure 4a is presented the left side of the compressed sample, where the displacement of aluminium occurred. The thickness of the aluminium in this part was 456.15 μ m, the steel was 710.13 μ m. As illustrated in Figures 4b–d, the thickness of the steel was 706.30 μ m or 710 μ m at the compressed part of the sample, while the thickness of the aluminium was 445.84 μ m or 474.27 μ m. Figures 4e and 4f show the thickness of the steel and aluminium on the uncompressed part of the sample. The

thickness of the steel was 706.75 μ m, while aluminium was 748.84 μ m.

At the sample 1.6 40.55 % deformation of the aluminium occurred, and the same as at the sample 1.2 and 1.5, no deformation of the steel occurred. Sample 1.6 was previewed under the

scanning electron microscope. Thickness and chemical composition of the intermediate layer was determined, resulting in the compression test of the sample 1.6. In Figure 5 presents the areas where the surface analysis of the sample 1.6 was done.



Figure 1: Thickness of the sample 1.5 after compression test: left compressed part (a), right compressed part (b), middle compressed part (c) and left uncompressed part (d).



Figure 2: EDS surface analysis of bonded part of the sample 1.5.



Figure 3: The thickness of intermediate layer in sample 1.5.

From Figure 5 it can be seen that the area 1, which presents the steel, contains amount fractions 0.750 % Si, 19.734 % Cr, 1.537 % Mn, 70.471 % Fe, 7.298 % Ni and 0.210 % Mo. Section 2 (intermediate layer) contains amount fractions 67.847 % Al, 0.284 % Si, 5.955 % Cr, 0.445 % Mn, 23.326 % Fe and 2.143 % Ni, while section 3 (aluminium) contains 99.454 % Al, 0.333 % Cr and 0.213 % Fe. The thickness of the intermediate layer that forms between the bonding of aluminium and steel was also measured and it was 5.84 μ m (Figure 6).

Using the Thermo-Calc programme, isoplete equilibrium phase diagram (Figure 7) for the intermediate phase was constructed, resulting in a sample 1.6. From the Figure 7 can be see that when the mass concentration of Fe is 36.174 %, following phases are possible: Al_8Cr_5 and $Al_{13}Fe_4$.

Second series

In the second series, where 6 compressing tests were made, profiled tool was used. In all sample no bond occurred.

Third series

In the third series 6 samples were compressed under certain conditions. Using an optical microscope, samples 3.3, 3.4 and 3.6 were analyzed. The bond occurred only at the sample 3.6, which was further analyzed using a scanning electron microscope. Sample 3.3 was heated to a temperature 540 °C, where it was held for 5 s so the temperature was homogeneous throughout the sample. This was followed by compressing the sample with a force of 23 kN. The displacement of the jaw was 0.4 mm. On Figure 8a it can be seen the part of a sample 3.3, which was compressed on the rib of the tool. The thickness of the aluminium in this part of the sample was 198 μ m, thickness of the steel was 468 μ m. Figures 8b and 8c shoe a part of the compressed sample, which was in the 'walley' of the tool. The thickness of aluminium on this part was 892 um (Figure 8b), while the thickness of the steel was 463 μ m (Figure 8c).

Sample 3.4 was heated to 540 °C where it was held for 5 s so the temperature was uniform throughout the sample. This was followed by pressing with a force of 22.5 kN. Rear calipers were set on 0.4 mm. Figure 9a shows a part of a sample 3.4, which was compressed by a rib of the tool. The thickness of the aluminium was 372 μ m and the steel 464 μ m. Figures 9b and 9c present the location where the material was compressed by a groove of the tool. Here the thickness of aluminium was 829 μ m (Figure 9b), the thickness of the steel was 467 μ m (Figure 9c).

Sample 3.6 was first heated to a temperature of 540 °C. At this temperature was held for 5 s and then pressed with a force of 16 kN, the displacement of the jaws was set to 0.6 mm. Figure 10 shows the bond between aluminium and steel in the sample 3.6.

In Figures 11a, b and c the thickness of aluminium and steel in specific parts of the sample can be seen. Figure 11a represents a part of the sample, which was compressed with a rib of the tool, Figures 11b and c represent a part of the sample, which is in the groove of the tool. Figure 11a shows that the thickness of the aluminium was in this case 334 μ m and steel 466 μ m. In Figure 11b the measured thickness of the steel, measured in Figure 11c was 464 μ m.

As the third series of compression tests lead to the bond only in the sample 3.6, it was further analyzed using a scanning electron microscope. In the sample the bond without an intermediate layer (Figure 12a) or with an intermediate layer (Figure 12b) was obtained, which was not continuous.

At the bond, without the intermediate layer surface and line analysis was made. The results of both analysis are shown in Figures 13 and 14.



Figure 4: Thickness of the sample 1.6: left compressed part (a) and (b), right compressed part (c), middle compressed part (d) and right uncompressed part (e) and (f).

From the results of the surface analysis shown in Figure 13 can be seen that the area 1 (aluminium) contains amount fractions 99.538 % Al, 0.003 % Si, 0.066 % Cr and 0.393 % Fe. Region 2, which represents the steel contains amount fractions 5.627 % Al, 0.224 % Si, 17.574 % Cr and 76.575 % Fe.

Results of surface analysis in Figure 14 show, that the area where an intermediate layer between aluminium and steel (section 1) was formed, contains amount fractions 45.569 % Al, 0.096 % Si, 10.134 % Cr and 44.201 % Fe. Region 2, which presents aluminium contains 99.378 % Al, 0.120 % Cr and 0.501 % Fe. The steel (section 3) contains amount fractions 6.079 % Al. 0.402 % Si. 17.204 % Cr and 76.315 % Fe.

Using Thermo-Calc program isoplete equilibrium phase diagram (Figure 15) for the intermediate layer was constructed, resulting in a sample of 3.6. From the diagram it can be seen that at the mass concentration of 58.4 % Fe, and 12.5 % Cr. phases AlCr2 and Al8Cr5 may occur. In all three series it was observed that the jaws on the Thermomechanical simulator of metallurgical stages Gleeble 1500 D are not completely parallel resulting in uneven bonds. On bonding a profiled tool had great impact. Due to the non-parallel jaw on which a tool for compression is placed, the force on certain points of the material is greater than elsewhere. This resulted in a different filling of the grooves of tools with aluminium. For the determination of the quality of the bond, further tests should be made such as bending tests or quantitative tensile tests of double-layered sheet.

Conc

0 382

18.603

1.531 wt.% 71.352 wt.% 7.766 wt.% 0.366 wt.%

100.000 100.000 wt.% Total



Figure 5: EDS surface analysis of bonded part of the sample 1.6.



Figure 6: The thickness of intermediate layer in sample 1.6.

2.	Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic %	Conc		
	Al	Ka	1,230.03	9.055	67.847	50.835	wt.%	
	Si	Ka	3.73	0.499	0.284	0.221	wt.%	
	Cr	Ka	151.10	3.174	5.955	8.598	wt.%	
	Mn	Ka	9.46	0.794	0.445	0.679	wt.%	
	Fe	Ka	432.81	5.371	23.326	36.174	wt.%	
	Ni	Ka	29.21	1.395	2.143	3.493	wt.%	
					100.000	100.000	wt.%	Total
3.	Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic %	Conc		
	A1	Ka	4 098 67	16 529	99 4 54	98 923	wt %	
	Cr	Ka	9.45	0.794	0.333	0.638	wt%	
	Fe	Ka	4 99	0.577	0.213	0.439	wt %	
			100,000		100.000	100.000	wt.%	Total

Error

Atomi

0.750 19.734

1.537

Intensity

(c/s) 2-sig %

10.54 0.838

30.21 1.419

84.72 2.377

6.56 0.661

1 164 42 8 811 70 471 7.298

THERMO-CALC (2013.01.31:11.41):AL-FE-(prerez6) DATABASE:COST2 P=1.01325E5, N=1, W(CR)=8.598E-2. W(SI)=2.21E-3,

W(MN)=6.79E-3, W(NI)=3.493E-2;

1.

Elt Line

Si Cr Mn Fe Ni Mo Ka Ka Ka Ka

La



Figure 7: Equilibrium isoplete phase diagram Al-Fe-Cr-Ni-Mn-Si.







Figure 8: The thickness of the material in the sample 3.3: rib of the tool (a) and in the 'valley' of the tool – aluminium (b) and steel (c).



Figure 9: The thickness of the material in the sample 3.4: rib of the tool (a) and in the valley of the tool – aluminium (b) and steel (c).



Figure 10: Bond in the sample 3.6.







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Figure 11: The thickness of the material in the sample 3.6: rib of the tool (a) and in the valley of the tool – aluminium (b) and steel (c).



Figure 12: The bond between AI 99.5 and ferrite stainless steel 1.4767 of the sample 3.6: there is no intermediate layer between the aluminium and steel (a) and discontinuous intermediate layer between the aluminium and steel (b).





Figure 14: EDS surface analysis of sample 3.6, where the intermediate layer occurred.



Masni procent Fe
Figure 15: Equilibrium isoplete phase diagram Al-Fe-Cr.

40 50

30

70 80

60

Conclusions

10 20

200

Ó

According to the results, it can be concluded:

- To achieve a good bond, the aluminium surface must be properly cleaned. Cleaning agent Nabadur 152 (5 %) ensures proper cleanliness of the surface of the aluminium so that the steel is not needed to be cleaned.
- The formation of the bond is heavily dependent on the geometry of the tool. The best results showed unprofiled tool. In the first series, where unprofiled tool was used two good bonds along the entire length of the sample were achieved. When the profiled tool was used, the bond only on a small area of the sample was achieved. Profiled tool should have shallower grooves and broad ribs.
- It is important to ensure parallelism of the jaw. Non-parallelism of the jaws causes a local increase in the forces leading to the formation of gaps and uneven filling of the grooves in the tools.
- In order to achieve the bond it is required compressing at a temperature of 550 °C or more. The time for holding the temperature for bonding should be at least 5 seconds.
- Minimum force required for the formation of the bond is 13 kN.
- The minimum deformation of the material, which is necessary for the formation of the connection, is 40.6 %.

 At the formation of the bond, intermediate laver was formed. The thickness of this layer depends on the holding time at the bonding temperature and the type of stainless steel. In the case of ferritic stainless steel with the same bonding conditions, a thinner intermediate layer than in austenitic stainless steel was obtained. The bond with the intermediate layer of 1 µm thick formed at a temperature of 540 °C and the holding time for 8 s. The composition of the intermediate layer is based on the ternary system Fe-Cr-Al. At the bonding of Al99.5 with ferrite or austenitic stainless steel the occurrence of the following phases is possible: Al₅Fe₂, Al₁₂Fe₄, Al₁₂Cr₂, $Al_{13}Fe_4$, $AlCr_2$ and Al_8Cr_5 .

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*AL8CR5_L *AL5FE2 *AL2FE

BCC B2#1

ALCR2

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Degradation of bitumen by Burkholderia cepacia KT803965 isolated from heavy oil impacted tropical soil

Razgradnja bitumna z mikroorganizmom Burkholderia cepacia KT803965, izoliranim iz tropskih tal, prepojenih s težko nafto

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Abstract

Non-conventional heavy oil including bitumen is fast replacing conventional light ones due to depletion of conventional oil reserves and high demand. Environmental pollution from its exploration and exploitation is of great global concern. Microorganisms remain a force in the remediation of oil polluted environment. This study investigated the degradation of bitumen by Burkholderia cepacia KT803965. Experiments were conducted as a function of temperature (20-50 °C), pH (3-11) and incubation period (2-10 d). The optical density was used as index of degradation and was measured using a UV-VIS spectrophotometer. The residual bitumen was analyzed using Gas Chromatography-Mass Spectrometry (GC-MS). The optimal process conditions of 40 °C, pH 7 after 13 d of incubation gave rise to the maximum biodegradation (optical density of 0.24). GC-MS result showed significant changes in chemical composition of the bitumen with generation of new compounds and elimination/ reduction of parent compounds owing to degradation. Some new degradation products identified were benzene (1-pentyloctyl), 23, 28-bisnor-17.β.(H)-hopane and 1,2-benzenedicarboxylic acid. This study revealed the excellent ability of *B. cepacia* KT803965 in degrading bitumen.

Key words: bitumen, Burkholderia cepacia KT803965, degradation, heavy oil, pollution

Izvleček

Zaradi izčrpanosti zalog in naraščajočega povpraševanja konvencionlno lahko nafto čedalje bolj nadomeščajo z nekonvencionalno težko nafto in bitumnom. Okoljsko onesnaževanje zaradi iskanja in črpanja teh surovin postaja že globalni problem. V rekultivaciji okolja, onesnaženega s težko nafto, se uveljavljajo tudi mikroorganizmi. V tem članku poročajo o raziskavi razgradnje bitumna z bacilom Burkholderia cepacia KT803965. V poskusih so preučevali odvisnost razgrajevanja od temperature (20-50 °C), pH (3-11) in inkubacijske dobe (2–10 d). Za indikator razgradnje so uporabili optično gostoto, ki so jo merili z UV-VIS-spektrofotometrom. Nerazpadli bitumen v tleh so določali s plinsko kromatografsko masno spektrometrično (GC-MS) metodo. Optimalne razmere pri postopku so ugotovili pri 40 °C in pH 7 po 13 d inkubacije, ko je bil dosežen maksimum biorazkroja pri optični gostoti 0,24. Določitve GC-MS kažejo v procesu razgradnje na izrazite spremembe kemizma bitumna z nastankom novih spojin in eliminiranjem/redukcijo izhodnih. Med novo nastalimi produkti razgradnje so ugotovili benzen (1-pentyloctyl), 23, 28-bisnor-17.β.(H)-hopan in 1,2-benzendikarboksilno kislino. S študijo so potrdili odlično uporabnost B. cepacia KT803965 za razgradnjo bitumna.

Ključne besede: bitumen, Burkholderia cepacia KT803965, razkroj, težka nafta, onesnaževanje

Introduction

The demand for crude oil worldwide has substantially increased which had resulted in straining the supply of conventional oil. This however, has led to consideration of alternative energy sources, among which are heavy oil and bitumen. These forms of oil are readily available to augment short and long-term needs ^[1].

The vast majority of heavy oils are a consequence of microbial alteration of oils in the reservoir ^[2] with more than 50 % of the world's oil occurring as biodegraded oils in heavy oil and tar sand accumulations ^[3]. These oils also represent a significant fraction of conventional oil reserves. According to Meyer et al. ^[1], there are about 3 396 billion barrels (539.6 × 10¹² L) of heavy oil in known accumulations and about 5 505 billion barrels (874.7 × 10¹² L) of bitumen resource in known accumulations in various basins around the world.

Gordon^[4] described unconventional oils as heavy, complex, carbon laden, and locked up deep in the earth, tightly trapped between or bound to sand, tar, and rock. Strausz et al.^[5] described bitumen as a thick, sticky form of crude oil, so heavy and viscous that it will not flow unless heated or diluted with lighter hydrocarbons. They may be immobile in the reservoir which typically requires upgrading to refinery feedstock grade^[1].

High demand for petroleum and associated products has substantially increased during the last ten decades which has made oil spills inevitable consequences of oil production and refining ^[6]. As a result, the problem of pollution during production and transportation of oil would remain a major environmental issue of great global concern ^[7]. Environmental hazards of bitumen exploration include destruction of ecosystem and pollution from bituminous toxic wastes ^[8]. While complete elimination of these problems is difficult to achieve, the aim is often to minimize environmental degradation ^[9].

The processes of removal of hydrocarbon pollutants from the environment involve physical, chemical and biological methods ^[10]. The biological method gains the upper hand due to inherent advantages of microorganisms. Bioremediation which is defined as any process that uses microorganisms or their enzymes to return the environment altered by contaminants to its original condition is an attractive process due to its cost effectiveness and the benefit of pollutant mineralization to carbon dioxide and water ^[11]. The ability of microorganisms to degrade pollutants and growth of cells are influenced by nutritional and environmental parameters such as carbon sources, nitrogen sources, inorganic salts, temperature, and pH ^[12]. Therefore, it is necessary to design an appropriate process of maximizing the degradation efficiency of bitumen by microorganisms. Burkholderia cepacia formerly known as Pseudomonas cepacia ^[13] has been reported to degrade crude oil ^[14, 15]. It has been shown to be capable of remarkable growth on aromatic fractions of crude oil ^[16, 17]. The organism has also been reported to grow on Polycyclic Aromatic Hydrocarbon (PAH) ^[18, 19] but it has not been reported to degrade bitumen. Since B. cepacia has been known to degrade PAH compounds, hence this study investigates the ability of the organism to degrade bitumen which contains heavy molecular weight hydrocarbons not reported from previous studies.

Materials and Methods

Collection of samples

Soil impacted with refined bitumen were collected randomly from Odeda, Osiele and Isolu, all in Odeda Local Government of Ogun State, while the bitumen used was obtained from Agbabu bitumen deposit in Odigbo Local Government of Ondo State, Nigeria. All samples were collected in triplicates. The unimpacted soil samples (control samples) were collected from the campus of Federal University of Agriculture, Abeokuta, Ogun State, Nigeria. Collection of soil samples was carried out as described by Balogun and Fagade ^[20]. Samples were collected in sterile aluminum foil and stored at 4 °C until used.

Total Heterotrophic Bacterial Count (*THBC*)

The total heterotrophic bacterial count was determined as described by Rahman et al. ^[21]. One gram of each of the samples was serially diluted five-fold in sterile distilled water and 1 mL of the diluents was aseptically dispensed into sterile Petri-dishes. Using the pour plate method, Plate Count Agar (Lab M, UK) was poured aseptically on inoculated plates. The plates were then incubated at 28 °C for 48 h.

Total Oil Utilizing Bacterial Count (TOUBC)

Oil utilizing bacterial count was carried out on Mineral Salt Medium (MSM) agar on which Dual Purpose Kerosene (DPK) was used as the sole carbon source. Prior to use, DPK was filtered using a Whatman filter paper No1 ^[22]. Agar (2 %) was added to solidify the medium. The MSM composition as described by Balogun and Fagade ^[23] was made up of Basal Salt Medium (BSM) and Trace element solution. The BSM contained (g L⁻¹): K₂HPO₄, 1.8; KH₂PO₄, 1.2; NH₄CL, 4.0; MgSO₄ · 7H₂O, 0.2; NaCl, 0.1; yeast extract, 0.1 and FeCl, ' 4H₂O, 0.05. Trace elements solution contained (g L⁻¹): H₂BO₂, 0.1; ZnSO₄ · 7H₂O, 0.1; CuSO₄ · 5H₂O, 0.05 and $MnSO_4$ · H₂O, 0.04 with the pH of 6.5. Ten mililitres of the trace elements solution was added aseptically to the sterilized basal salt medium to make it up to 1 L. One mililitre of the serially diluted samples was aseptically dispensed into sterile Petri-dishes using the pour plate method.

Surface Active Bacterial Count (SABC)

Screening for surface-active bacteria was carried out on blood agar as described by Tabatabaee et al. ^[24]. The blood agar was made up of nutrient agar containing volume fraction 5 % defibrinated rabbit blood. One millilitre of the serially diluted sample was plated on the blood agar using the pour plate method. The plates were incubated at 28 °C for 48 h after which the colonies that showed clear zone of red blood β -heamolysis were counted as surface active agent producer.

Screening test for the utilization of bitumen

Bacterial isolates were tested for their potential to utilize bitumen as carbon source as described by Bidoia et al. (2010). Pure strain was inoculated into 7.5 mL of MSM incorporated with 1 g of bitumen. Then, 40 μ L of 2, 6-Dichlorophenol Indophenol (DCPIP) was added and incubated at 37 °C for 60 h. Absorbance of the medium at 600 nm was measured at intervals of 24 h for 5 d using a digital colorimeter (Jenway 6051, UK).

Characterization of bacterial isolates

The isolate was identified on the basis of its colonial morphology, cellular morphology and biochemical characterization of the isolate was done using API 20E identification kit (Biomérieux, France). API 20E kit was used according to the manufacturer's instruction. The organism was further characterized using 16S rRNA. The PCR amplification of 16S rRNA gene, from the purified genomic DNA was carried out using universal primer sets. Sequencing of the gene was done and identification of the sequence was by Basic Local Alignment Search Tool (BLAST) with National Center for Biotechnology Information (NCBI) gene data base. The sequence was also deposited at the NCBI database.

Bitumen degradation experiment

The experiment was conducted according to the Critical Control Design (CCD) of Design Expert 7.0. (Stat-Ease Inc., USA). Three independent factors of temperature, pH and experimental time and optical density (dependent response variable) were considered. The complete design consisted of 20 experimental points which included 6 replications at the central point based on the pattern generated through the software. Growth of the isolate was monitored in 250 mL Erlenmeyer flasks containing 99 mL MSM with 1 g of bitumen as carbon substrate. The optical density at 600 nm of the inoculum was adjusted to 0.5 using a spectrophotometer (Uniscope SM 7504 model, UK) before seeding into each flask. The optical density (OD₆₀₀) of replicates readings was used as the degradation index ^[6, 25]. Control flasks were also set up in similar manner but without seeding with the isolate.

Gas chromatography- Mass Spectrometry (GC-MS) analysis

The residual and the undegraded (control) bitumen were extracted from the culture fluid with 50 mL aliquots of dichloromethane (DCM) in a separating funnel. The organic phase was drawn off and concentrated. The concentrated extracts were fractionated on glass column packed with silica and alumina (2:1) into aliphatic, aromatic, and polar fractions by successive elution with 20 mL of hexane, 70 mL of hexane/DCM (7:3) and 25 mL of methanol respectively ^[26]. The aromatic fractions were further concentrated to 0.5 mL for GCMS analysis. The GC system (Agilent Technologies 7890A model) used for the analysis was equipped with Mass spectrometer detector 5975C (VLMSD) and injector (Auto) 7683B series. HP-5 Agilent technologies installed with an HP-DB5 column (length 30 m, 320 µL I.D., and 0.25 µm film thickness). Helium gas was used as carrier gas. The mass spectrometer was operated in the electron impact mode at 70 eV. The aromatic fractions were injected with an auto sampler in the splitless/split mode with a split time of 1 min after injection and the injector temperature was 280 °C. Column temperature was programmed from 50 °C (held for 1 min) to 150 °C at a rate of 10 °C/min, then to 210 °C at a rate of 2 °C/min and finally to 280 °C (held for 7 min) at a rate of 35 °C/min. Compound identification was based on the robust 2011 National Institute of Standards and Technology library by noting only compounds with over 50 % library matching.

Statistical analysis

A functional factorial design was applied to derive a statistical model for the effects of the cultural conditions on degradation of bitumen by *B. cepacia* using CCD and to identify the combination of factors that would lead to the enhancement of degradation. The statistical software package was used for regression analysis and graphical analysis of the data obtained during the experiment. Analysis of variance (ANOVA) was used to estimate the statistical parameters. The significance of the model equation and model terms were evaluated by F-test. The quality of fit of the polynomial model equation was expressed by the coefficient of determination (R^2), adjusted R^2 and adequate precision. The fitted polynomial equation was expressed as three-dimensional surface plots to visualize the relationship between the responses and the experimental levels of each factor used in the design.

Results

The results of the total heterotrophic bacterial count (THBC) and total oil utilizing bacterial count (TOUBC) from bitumen impacted and unimpacted soil (Table 1) showed that the THBC ranged from 1.6×10^5 CFU g⁻¹ to 2.0×10^6 CFU g⁻¹ with Odeda having the highest bacterial counts. The sample from Odeda had the highest total oil utilizing bacterial count (TOUBC) of 3.6×10^5 CFU g⁻¹ while the lowest counts of 1.5×10^4 CFU g⁻¹ was recorded at FUNAAB. Surface active bacterial counts from Isolu had the highest of 6.5×10^4 CFU g⁻¹ to the least count of 1.0×10^4 CFU g⁻¹ obtained at Osiele.

It was obtained from the screening procedure that *B. cepacia* KT803965 was able to utilize bitumen in the presence of DCPIP in the shortest possible time and was therefore used for the degradation of bitumen. The rate and extent of colour change of DCPIP from blue to colourless with time revealed the potential of the isolates to utilize the hydrocarbon tested as a carbon source.

The bacterium B. cepacia isolated from bitumen impacted soil from Agbabu is a Gram-negative rod with ability to oxidize glucose, mannitol, inositol, sorbitol and rhamnose. It is oxidase positive, liquefied gelatin, grew on citrate and MacConkey agar and positive for arginine dihydrolase, and catalase. However the organism test negative for Voges-Proskauer, indole, urease, hydrogen sulphide, amygladin oxidation, ornithine decarboxylase and lysine decarboxylase. The 16S rRNA identification of the isolate revealed that, B. cepacia KT803965 is closely related (99 % similarity) to Burkholderia cepacia ATCC 25416 with accession number CP007746.1. The sequence of *B. cepa*cia KT803965 has been deposited at the NCBI gene bank database.

The degradation experimental design is presented in Table 2. The optimum response of 0.24 was observed at temperature of 40 °C and pH 7 after 13 d of incubation. The central points have optical densities that ranged between 0.16 and 0.17 at 40 °C and pH 7 after 6 d of incubation. The lowest response of 0.004 was obtained at zero hour of incubation at 40 °C and pH of 7.

S/N	Sample collection location	Coordinates	THBC (× 10 ⁴ CFU g ⁻¹)	TOUBC (× 10 ⁴ CFU g ⁻¹)	SABC (×10 ⁴ CFU g ⁻¹)			
	Heavy oil impacted soil							
1	Odeda	7.23119 N 3.52687 E	205.0 ± 7.1^{b}	36.0 ± 5.7^{b}	3.2 ± 0.3^{bc}			
2	Osiele	7.23278 N 3.52294 E	23.50 ± 2.1^{a}	4.5 ± 0.7^{a}	1.0 ± 0.0^{a}			
3	Isolu	7.20425 N 3.44136 E	19.3 ± 1.1^{a}	7.0 ± 1.4^{a}	6.5 ± 0.7^{d}			
	Natural bitumen deposit							
4	Agbabu	6.35253 N 4.49547 E	16.8 ± 1.8^{a}	7.5 ± 0.7^{a}	4.5 ± 0.7^{cd}			
	Heavy oil unimpacted soil							
5	Funaab	7.22844 N 3.43618 E	16.0 ± 2.8^{a}	1.5 ± 0.7^{a}	2.0 ± 1.4^{ab}			

Table 1: Bacterial counts from various sampling points

Values are means of replicate readings \pm standard error

Mean values with same letter within a column are not significantly different at p < 0.05

THBC: Total Heterotrophic Bacterial Count

TOUBC: Total Oil Utilizing Bacterial Count

SABC: Surface Active Bacterial Count

Table 2: Central composite design matrix measured and predicted response

Order		Factors			Response	
	A: Temperature /°C	B: pH	C: Time /Day	Experimental value (Actual)	Predicted	Residual (Actual - predicted)
1	30.00	3.00	2.00	0.025	0.022	3.051E-003
2	40.00	7.00	0.00	4.000E-003	0.044	-0.040
3	40.00	7.00	6.00	0.17	0.17	3.070E-003
4	40.00	7.00	6.00	0.16	0.17	-1.930E-003
5	40.00	7.00	6.00	0.17	0.17	2.070E-003
6	40.00	7.00	6.00	0.17	0.17	1.070E-003
7	30.00	3.00	10.00	0.095	0.11	-0.011
8	23.18	7.00	6.00	0.094	0.11	-0.015
9	30.00	11.00	10.00	0.12	0.13	-7.612E-003
10	50.00	3.00	2.00	7.000E-003	2.385E-003	4.615E-003
11	50.00	11.00	10.00	0.16	0.17	-6.048E-003
12	50.00	11.00	2.00	0.045	0.037	7.887E-003
13	40.00	7.00	6.00	0.17	0.17	2.070E-003
14	50.00	3.00	10.00	0.055	0.096	-0.041
15	40.00	13.73	6.00	9.000E-003	0.030	-0.021
16	40.00	0.27	6.00	4.000E-003	-0.021	0.025
17	40.00	7.00	6.00	0.17	0.17	1.070E-003
18	30.00	11.00	2.00	0.052	0.014	0.038
19	56.82	7.00	6.00	0.14	0.12	0.019
20	40.00	7.00	12.73	0.24	0.20	0.036

Values are means of replicate readings

E: Exponential

Compound Name
Benzene, (1-butyloctyl)
Benzene, (1-propylnonyl)
Benzene, (1-methyldodecyl)
Ambrosin
Azulene, 1,2,3,4,5,6,7,8-octahydro-1,4-dimethyl-7-(1-methylethenyl)- , [1s-(1.alpha.,4.alpha.,7.alpha.)
1,2-benzenedicarboxylic acid
2,2,4-Trimethyl-3-(3,8,12,16-tetramethyl-heptadeca-3,7,11,15-tetraenyl)-cyclohexanol
23,28-Bisnor-17.beta.(H)-hopane

Table 3: Identified products released during the degradation process by B. cepacia

Table 4: ANOVA for response surface quadratic model

Source	Sum of squares	Degree of freedom	Mean square	F value	P value Prob > F
Model	0.092	9	0.010	12.71	0.0002
А	1.643E-004	1	1.643E-004	0.20	0.6605
В	3.120E-003	1	3.120E-003	3.89	0.0768
С	0.036	1	0.036	45.31	< 0.0001*
AB	9.245E-004	1	9.245E-004	1.15	0.3082
AC	5.000E-005	1	5.000E-005	0.062	0.8079
BC	5.780E-004	1	5.780E-004	0.72	0.4158
A ²	4.714E-003	1	4.714E-003	5.88	0.0358*
B ²	0.047	1	0.047	58.87	< 0.0001*
C ²	4.437E-003	1	4.437E-003	5.53	0.0405*
Residual	8.020E-003	10	8.020E-004	-	-
Lack of Fit	8.005E-003	5	1.601E-003	539.65	< 0.0001*
Pure Error	1.483E-005	5	2.967E-006	-	-
Corrected Total	0.100	19	-	-	-
R ²	0.9196				
Adjusted R ²	0.8473				

* = significant model terms A: Temperature B: pH C: Time R2: Coefficient of determination E: Exponential The response surface plot showed that the optical density increases with increase in temperature and pH. The highest optical density of 0.24 was obtained at 40 °C and pH 7 while the lowest optical density of 0.004 was obtained at the same temperature and pH after inoculation. Beyond this temperature and pH, there are further decreases in optical density (Figure 1).



Figure 1: Surface and contour plot showing effect of temperature and pH on bitumen degradation (optical density).



Figure 2: Surface and contour plot showing the effect of temperature and time on bitumen degradation (optical density).

Figure 2 show the plot of temperature and time against optical density. The optical density increases with time. The highest optical density of 0.24 was obtained after 13 d of incubation while the least optical density of 0.004 was obtained on the zero day of incubation.

Microorganisms serve as an important tool for the simultaneous biodegradation and release of valuable compounds during the degradation. Identified degradation products formed during the degradation process are shown in Figure 3. The analysis of variance was performed in order to verify the validity of the models and the results were presented in Figure 4. According to the analysis of variance, *F*-value (12.71) for the overall regression model is significant (p > 0.05) and the lack of fit is significant indicating that the model with interaction is inadequate in approximating the response surface of the experimental design. The regression analysis of the experimental design showed that C, A^2 , B^2 , C^2 are significant model term (p < 0.05). The predicted R^2 of 0.3947 is not as close to the adjusted R^2 of 0.8473 as one might normally expect. This may indicate a large block effect between the experimental and the predicted values. Adequate precision measures the signal to noise ratio and a ratio greater than 4 is desirable. In this case, a ratio of 11.099 was achieved indicating an adequate signal and so this model can be used to navigate the design space.

The GC-MS results showed significant variations among the studied degradation and control sample in the analyzed aromatic fractions. Table 3 showed the degraded compounds and new compounds that were detected. Benzene, (1-butyloctyl), benzene, (1-propylnonyl) and benzene, (1-methyldodecyl) were some of the degraded products while ambrosin and azulene are some of the new products detected.



Figure 3: Surface and contour plot showing the effect of pH and time on bitumen degradation (optical density).

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Figure 4: The Total lon Chromatogram (TIC) of the control sample and the extracts of the residual degraded bitumen.

Discussion

This study showed high bacteria counts in all the locations. The counts are consistent with the works of Obayori et al. ^[15] and Wang et al. ^[27] that reported similar bacterial counts from hydrocarbon-polluted site. The range of THBC recorded in this study is consistent with the findings of Jennings and Tanner ^[28]. The high THBC recorded in unimpacted soil is due to the high level of organic matter usually present in fallow uncultivated soil which supports the growth of microorganisms. The enumeration of TOUBC is an important criterion for the determination of potential for microbial degradation of oil contaminated environments, and to assess the amount of oil pollution that has occurred ^[29].

The distribution of bacterial isolates obtained from various sampling sites indicates common occurrence of metabolically active strains contaminated with hydrocarbon suggesting the ability of the microorganisms to utilize these hydrocarbon as a carbon and energy source. The ability to utilize hydrocarbon substrate is exhibited by a wide variety of bacteria genera ^[30] that is widely distributed among oil polluted as well as pristine soils [31, 32]. Some general trends have indicated that Gram negative Proteobacteria group is major hydrocarbon utilizers ^[33, 34]. These groups were usually associated with degradation and their abundance was positively correlated to hydrocarbon utilization ^[34].

Screening of organisms that produce surface active agent had been done previously by several researchers using haemolytic activity test ^[24, 35]. The organism produced surface active agents and thus has the ability to produce biosurfactant which enhances degradation.

Environmental conditions such as temperature and pH have been observed to influence the rate of biodegradation ^[7, 8]. The effect of temperature and pH has also been found to influence the biodegradation of phenol ^[36, 37]. The physical conditions under which microorganisms acts on a substrate govern the speed and efficiency of its action ^[38], thus, the effect of temperature, pH and time were investigated in relation to the growth of the test organism on bitumen substrate. Differences in response of the organism with different conditions of temperature, pH and time also indicate fundamental differences in the mechanisms of bitumen oxidation ^[38]. The optimum temperature of 40 °C and pH 7 obtained in this study agrees with what was reported by Olabemiwo et al. [7] and Adebayo et al. [8] while working on solubilized bitumen. It is expected that biodegradation rates will be enhanced to a certain extent, typically in the range of 30 °C to 40 °C [39]. Above 40 °C, the membrane toxicity of hydrocarbon to microorganisms is increased, thus hindering biodegradation ^[40]. Degradation rates are highest at near neutral pH^[41]. This implies that bitumen degradation is possibly more effective at neutral or slightly alkaline pH condition. This is in agreement with Sonawdekar^[42] which found out that bacteria are able to grow on hydrocarbon at that pH range.

It was proven from this study that incubation time (p < 0.05) played crucial role in the degradation process. The convex response surface suggested well-defined optimum variables of temperature and pH and that the degradation increased with increase in temperature and pH up to 40 °C and 7 respectively and then declined with further increase of these two parameters. The aromatic fraction was considered for analysis due to the fact that the fraction is expected to have much impact on degradation. Comparing the degradation results with the control sample, a significant number of the precursor compounds found in the bitumen have been degraded (Figure 4). In most cases the compounds were not found in the extracts of the residual bitumen. It was difficult to quantify the amount of individual compound degraded since individual standards of the compounds

were not available. However, using their relative abundance (peak areas) we were able to ascertain the level of degradation for most of the compounds (Figure 4).

The control sample has over two hundred compounds with a significant proportions identified with very high abundance. Nine major compounds were recorded as degradation products as recorded in the residual bitumen sample by *B. cepacia* KT803965. This is highly significant indicating the potency of this isolate in degrading and utilizing heavy molecular weight organic compounds ^[43]. Since bitumen contain Polycyclic Aromatic Hydrocarbons (PAH)^[44], the aromatic fractions of the residual bitumen were significantly degraded by the organism. The control sample assisted in establishing the extent of degradation among the various degraded compounds. The results obtained showed that under conditions of reduced availability of a certain class of compounds, microorganisms opt for those that are, although less biodegradable but more accessible substrate. In this case, the reason for lower biodegradability might be the smaller amounts of *n*-alkanes in the pollutant ^[45].

However, some compounds such as (1-methylundecyl) benzene and (1-butylheptyl) benzene showed very high resistant to degradation as they were not amenable to degradation but with further timing and optimization, these compounds could be further degraded.

Conclusion

The method employed in this study can be successfully applied to determine the potential of organism in the degradation of bitumen. The optimal conditions obtained in this study laid a solid foundation for further use of this microorganism in the treatment of heavy oil polluted environment.

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CO₂ temporary storage in big underground caverns

Začasno skladiščenje CO₂ v velikih podzemnih kavernah

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Abstract

After the CO₂ has been captured at the source of emission, the CO₂ would have to be transported to the storage site using different technologies. In some countries (i.e. USA) real possibilities exist so that available and new oil and water pipe lines could be used for such operations. In practice it means that transportation could be carried out with motor carriers, railway and water carriers. If the present experiences are taken into account and the real situation checked, such transportation systems are mainly used in praxis. For maximum throughput and to facilitate efficient loading and unloading, the physical condition with respect to pressure and temperature for the CO₂ should be the liquid or supercritical/dense phases. Temporary storage of CO₂ is of importance for finding a comprehensive solution for long-term storage under various environmental circumstances. Underground caverns are one of the possibilities of temporary storage. Geotechnical analysis of stress and strain changes that are present in the rocks around underground caverns filled with CO₂ under high pressure provides a realistic assessment of conditions for temporary storage. This paper presents the analysis described above, for different parameters relating to underground storage of CO₂.

Key words: temporary storage, big underground caverns, numerical modelling, boundary element method – BEM, CO₂ high-pressure

Izvleček

Po zajemu CO_2 , ki ni namenjen izpustu v atmosfero, je več možnosti transportiranja večjih količin tega plina v skladišče. V nakaterih državah (npr. ZDA) je realna možnost za transport CO_2 uporaba obstoječih ali novih cevovodov za oskrbo območij z ogljikovimi derivati. Prav tako je v delu več projektov, ki upoštevajo navedeno možnost transporta CO_2 v Severnem morju. Predlogi za transport CO_2 s cestnimi, železniškimi in vodnimi transportnimi sistemi, ki jih je mogoče prilagoditi posebnim zahtevam, upoštevajo specifične lastnosti CO_2 , saj bi bila najbolj ekonomična cena transporta na enoto dosežena, če bi bil plin v tekoči oz. superkritični gosti fazi.

Začasno skladiščenje CO_2 ima velik pomen pri iskanju celovite rešitve dolgoročnega skladiščenja v različnih okoljih. Podzemne kaverne so ena izmed možnosti začasnega skladiščenja. Geotehnična analiza napetostnih in deformacijskih sprememb, ki so v hribinah okrog podzemnih kavern, napolnjenih s CO_2 pod visokimi tlaki, omogoča realno oceno razmer začasnega skladiščenja. V prispevku je prikazana navedena analiza za različne parametre začasnega podzemnega skladiščenja CO_2 .

Ključne besede: začasno skladišče, velike podzemne kaverne, numerično modeliranje, metoda mejnih elementov – BEM, visok tlak CO₂

Introduction

Carbon dioxide (CO_2) is a greenhouse gas that occurs naturally in the atmosphere. Human activities, such as the burning of fossil fuels and other processes, are significantly increasing its concentrations in the atmosphere, thus contributing to the Earth's global warming. One technique that could limit CO₂ emissions from human activities into the atmosphere is CO₂ capture and storage (CCS). It involves collecting, at its source, the CO₂ that is produced by power plants or industrial facilities and storing it away for a long time in underground geological layers, in the oceans, or in other materials. It should not be confused with carbon sequestration, which is the process of removing carbon from the atmosphere through natural processes such as the growth of forests. It is expected that fossil fuels will remain a major energy source until at least the middle of this century^[1-5]. Therefore, techniques to capture and store the CO₂ produced, combined with other efforts, could help stabilise greenhouse gas concentrations in the atmosphere and fight climate change. CO₂ could be captured from power plants or industrial facilities that produce large amounts of it ^[6-9]. Technology for CO₂ capture from small or mobile emission sources, such as home heating systems or cars, is not sufficiently developed yet. The question is whether it could be realised in the near future? A significant proportion of the CO₂ produced by fossil fuel power plants could potentially be captured. By 2050 the amount captured could represent 21 % to 45% of all the CO₂ emitted by human activities. After the CO₂ has been captured at the source of emission, the CO₂ would have to be transported to the storage site. Such transportation would require large scale infrastructures due to the large volumes to be handled. Nowadays existing CO₂ transportation systems has its basic location in the USA, where several million tons of CO₂ are transported annually, over long distances on shore in high pressure pipelines for use in the EOR industry (Gale et al. 2002)^[10]. Using CO₂ in EOR (Enhanced Oil Recovery) projects has the advantage of adding a value to the CO₂, e.g. oil producers in the USA are willing to pay between 9 US\$/t and 18 US\$/t of »end of pipe« delivered CO₂. Pipelines for off-shore

transportation of CO₂ have not been applied yet but are technologically feasible today, and a CO₂ pipeline infrastructure-off shore was investigated in the CO₂ for EOR in the North Sea (CENS) project^[11]. In practice it means that transportation could be carried out with motor carriers, railway and water carriers. If the present experiences take into account and check the real situations, such transportation systems are mainly used in the food and brewery industry, and the amounts transported are within the range of some 100 000 t of CO₂ annually, so that is much smaller than the amounts associated with Carbon Capture and Storage (CCS) (Figure 1). In contrast the transportation conditions for CO₂ have some similarities with LPG (Liquefied Petroleum Gas) technologies, which are transported by water carriers, railway and motor carriers on a relatively large scale. Hence, from these points of view, experiences from the LPG industry could also be used for establishing a large scale CO₂ transportation infrastructure. For maximum throughput and to facilitate efficient loading and unloading, the physical conditions with respect to pressure and temperature for the CO₂ should be the liquid or supercritical/ dense phases. It should be noted that pipelines suffer from pressure drops along the transportation route, which can result in two phase flows and operational and material problems (e.g. cavitation) in components such as booster stations and pumps. Utilising pipelines still needs stable conditions of operation where the transported media is in the supercritical/dense phase^[12-15]. This condition occurs at temperatures higher than 60 °C and pressures above the critical pressure of 7.38 MPa, giving a good margin for avoiding two phase flows. For the other means of transportation, i.e. motor carriers, railway and water carriers, which have constant pressure, liquid conditions are suitable. The density for CO₂ approaches 1 000 kg/m³ as liquid, as well as during the supercritical/dense phase.

If available conditions are weighted in the goal to find optimal technical solutions the intermediate storage can be usable in different ways. A pipeline has the advantage of providing steady state flow, i.e. a continuous flow from the emission source to the final storage site. That means the complex transportation system should include appropriate intermediate storage facilities for handling the reloading of CO₂ at the middle points or at the final point close to harbour's facilities. There are two main technologies for intermediate storage of LPG, either underground in great rock and salt caverns or in large steel tanks above ground which have many disadvantages. But at present, only the steel tank technology is used for CO₂, in the contra version that both technologies can be applied in practice. Existing rock caverns for LPG have storage capacities up to around 500 000 m³, which should approximately correspond to $500\,000$ t of CO₂. In the other hand salt caverns have similar storage capacities of LPG but are excluded in this work due to uncertainties with respect to the dissolution behaviour of CO₂. Steel tanks have storage capacities up to 3 000 t of CO₂^[12, 13]. Rock caverns within the LPG industry are constructed in two different ways, either as pressurised or as cooled caverns. If the caverns are intended for storage of CO₂, these techniques must be combined to create favourable conditions with respect to pressure and temperature for the CO₂. So, the construction cost of rock shelter depends mainly on the rock quality, which is available at the decided location. Low bearing capacity of *»poor* rock quality« increases the need for strong support measures which include lining and reinforcement of the rock strata. In those cases nonlinear increases in costs should be expected. In many technical and scientific studies the safety and public acceptance are not included enough. CO₂ is not toxic but can be fatal, due to asphyxiation, at concentrations exceeding around 10 % by volume ^[16], levels that can be achieved at a discharge as CO₂ is heavier than air and, hence, will tend to collect in depressions. Statistics from the EOR industry clearly show that the risks for pipeline leakage are lower than for natural gas or hazardous pipelines. Anyway in the goal to minimise risks, transportation of CO₂ should be routed away from large centres of population. Another issue, which can indirectly affect the transportation, is the public opinion concerning storage of CO_2 . The concept of off shore disposal on average is considered to be safer, if the leakage is under question, than on shore systems. For this reason the support of the public is more easily implemented for the off shore system ^[14, 15, 17-19]. The above facts and assessing the need for the construction and use of temporary CO₂ storage are the basis for further work in this specialised field of underground construction. Already in several sentences it has also been suggested that the appropriate price for the construction of underground structures, essential important geological, hydrogeological and geotechnical conditions should be present at the selected location. Within the scope of the presented work the addition of the basic features of the behaviour of CO₂, given orientation are necessary and analysis of some possible construction of temporary underground storage facilities. In the analyses should take into account the economic viability of the storage of CO₂ at pressures between 80 bar and 100 bar at the ambient temperature of rock mass. It is possible to take into account the technological requirements of CO₂ transport in terms of maintaining the highest possible density of CO₂ in the liquid state, which is an economically important item for establishing the final price of permanent storage of CO₂^[20-23].

Some information about CO₂ producers

Coal power plants are a good example of a large point source of CO₂ emissions. Three systems are available for power plants: post-combustion, pre-combustion, and oxfuel combustion systems. The captured CO₂ must then be purified and compressed for transport and storage. It is possible to reduce the CO₂ emissions from new power plants by about 80 % to 90 % but this increases the cost of electricity produced by 35 % to 85 %. For industrial processes where a relatively pure CO₂ stream is produced, the cost per ton of CO₂ captured is lower. Except when the emission source is located directly over the storage site, the CO_2 needs to be transported. Pipelines have been used for this purpose in the USA since the 1970s. CO₂ could also be transported in liquid form in ships similar to those transporting liquefied petroleum gas (LPG). For both pipeline and marine transportation of CO₂, costs depend on the distance and the quantity transported. For pipelines, costs are higher when crossing water bodies, heavily congested areas, or mountains. Compressed CO₂ can be injected into porous rock formations below the Earth's surface using many of the same methods already used by the oil and gas industries (Figure 1). The three main types of geological storage are oil and gas reservoirs, deep saline formations, and un-minable coal beds [24-28]. CO₂ can for instance be physically trapped under a well-sealed rock layer or in the pore spaces within the rock. It can also be chemically trapped by dissolving in water and reacting with the surrounding rocks. The risk of leakage from these reservoirs is rather small. Storage in geological formations is the cheapest and most environmentally acceptable storage option for CO_2 . Oceans can store CO_2 because it is soluble in water. Captured CO₂ could potentially be injected directly into deep oceans and most of it would remain there for centuries. CO₂ injection, however, can harm marine organisms near the injection point. It is furthermore expected that injecting large amounts would gradually affect the whole ocean. CO₂ storage in oceans is generally no longer considered as an acceptable option. Through chemical reactions with some naturally occurring minerals, CO₂ is converted into a solid form through a process called mineral carbonation and stored virtually permanently. This is a process which occurs naturally, although very slowly. These chemical reactions can be accelerated and used industrially to artificially store CO₂ in minerals. However, the large amounts of energy and mined minerals needed make this option less cost-effective. It is technically feasible to use captured CO₂ in industries manufacturing products such as fertilisers. The overall effect on CO₂ emissions, however, would be very small because most of these products

rapidly release their CO₂ contents back into the atmosphere. It is expected that carbon capture and storage would raise the cost of producing electricity by about 20 % to 50 % but there are still considerable uncertainties. In a fully integrated system including carbon capture, transport storage and monitoring, the capture and compression processes would be the most expensive steps. Geological storage is estimated to be cheaper than ocean storage, the most expensive technology being mineral carbonation. Overall costs would depend both on the technological choices and on other factors such as location or fuel and electricity costs. Capture and storage of the CO₂ produced by some industrial processes such as hydrogen production can be cheaper than for power plants.

Basic physical and chemical parameters of CO₂

CO₂ is a naturally-occurring substance made up of carbon and oxygen, two of the more common chemical elements on earth. Under normal atmospheric conditions, CO₂ is a gas. It can be compressed into a liquid, frozen into a solid (dry ice) or dissolved in water (carbonated beverages, beer and sparkling wines) (Figure 2). In the atmosphere, CO₂ comprises about 0.04 % of the air we breathe. It also occurs naturally in both fresh and sea water, and in the ground Meanwhile, green plants absorb CO₂ for photosynthesis and emit oxygen back into the atmosphere CO₂ is also exchanged between the atmosphere and the oceans and is emitted or absorbed in other natural processes. Working together in a natural system called the carbon



Figure 1: Possible CO₂ capture and storage – CCS system^[12].



Figure 2: Crystal structure of dry ice and sample of solid carbon dioxide or »dry ice« pellets and arising atmospheric carbon dioxide versus time^[29].

cycle; these processes have in the past kept the levels of CO_2 in the atmosphere stable over time. Nature's carbon cycle normally keeps CO_2 levels in balance but human activity, mostly the burning of fossil fuels, produces more CO_2 than nature can absorb. The arrows in this diagram show the annual flows of carbon in billion tones (metric tons). The human contribution is relatively small but enough to throw the cycle off balance. The extra CO_2 stays in the atmosphere, where it causes global warming. CO_2 is a greenhouse gas. That is, its presence in the atmosphere traps heat energy from the sun. This keeps the climate warm enough for life to continue.

As atmospheric CO_2 levels increase from natural levels the climate becomes warmer, changing the natural balance in most parts of the world. This has a wide range of major disruptive impacts on the environment, natural resources and human communities throughout the world. Living things consist largely of water and molecules containing carbon. When fuels derived from living things such as wood or fossil fuels (oil, coal or natural gas) are burned, the carbon combines with oxygen to form CO_2 that is released into the atmosphere. People haven't thrown the natural carbon cycle out of balance by burning fossil fuels (Figure 3). More CO_2 is now entering the atmosphere than can be naturally absorbed, contributing to global warming.

Chemical and physical characteristics of CO₂

 CO_2 is one of the gases in our atmosphere, being uniformly distributed over the earth's surface at a concentration of about 0.033 % or 330×10^{-6} . Commercially, CO₂ finds uses as a refrigerant (Figure 2, dry ice is solid CO₂), in beverage carbonation, and in fire extinguishers. Because the concentration of carbon dioxide in the atmosphere is low, it is impractical to obtain the gas by extracting it from air. Most commercial carbon dioxide is recovered as a by-product of other processes, such as the production of ethanol by fermentation and the manufacture of ammonia. Some CO₂ is obtained from the combustion of coke or other carbon-containing fuels. Carbon dioxide is released into our atmosphere when carbon-containing fossil fuels such as oil, natural gas, and coal are burned in air. As a result of the tremendous world-wide consumption of such fossil fuels, the amount of CO_2 in the atmosphere has increased over the past century, now rising at a rate of about 1×10^{-6} per year. Major changes



Figure 3: Image courtesy of CO_2 CRC, with values of carbon fluxes and sinks sourced from NASA Earth Science Enterprise and the International Energy Agency^[12].

in global climate could result from a continued increase in CO₂ concentration. In addition to being a component of the atmosphere, carbon dioxide also dissolves in the waters of the oceans. As carbon dioxide dissolves in sea water, the equilibrium is established involving the carbonate ion, CO_3^{2} . The carbonate anion interacts with cations in seawater. According to the solubility rules, »all carbonates are insoluble except those of ammonium and Group IA elements.« Therefore, the carbonate ions cause the precipitation of certain ions. For example, Ca²⁺ and Mg²⁺ ions precipitate from large bodies of water as carbonates ^[2]. Carbon dioxide does not exist in liquid form at atmospheric pressure at any temperature. The pressure-temperature phase diagram of CO₂ shows that liquid carbon dioxide at 20 °C requires a pressure of 30 bar (Figure 4). The lowest pressure at which liquid CO_2 exists is at the triple point, namely 5.11 bar at -56.6 °C. At the critical point (31.1 °C, 73 bar - located upper right in the phase diagram for CO₂), the temperature and pressure at which the liquid and gaseous phases of a pure stable substance become identical.

The high pressures needed for liquid CO_2 require specialised washing machines. Clothing is immersed in liquid CO_2 in a highly pressurised cylinder and agitated by high-velocity fluid jets to remove soils, then dried in a high-velocity spin cycle. Liquid CO_2 has drawn high marks in Consumer Reports' tests for its cleaning results, and it is environmentally-friendly as it produces no chlorinated pollutants.

Practical CO₂ storage capacities

The theoretical CO₂ storage capacity represents the mass of CO₂ that can be stored in hydrocarbon reservoirs assuming that the volume occupied previously by the produced oil or gas will be occupied in its entirety by the injected CO₂. The effective CO₂ storage capacity represents the mass of CO₂ that can be stored in hydrocarbon reservoirs after taking into account intrinsic reservoir characteristics and flow processes, such as heterogeneity, aquifer support, sweep efficiency, gravity override, and CO₂ mobility. However, there are also extrinsic criteria, which need consideration when implementing CO₂ storage in oil and gas reservoirs on a large scale and that further reduce the CO₂ storage capacity in oil and gas reservoirs to practical levels. The storage capacity of oil reservoirs undergoing water flooding is significantly reduced, making it very difficult to assess their CO₂ storage capacity in the absence of detailed, specific numerical simulations of reservoir performance. It is very unlikely that these oil pools, and generally commingled pools, will be used for CO_2 storage, at least not in the near future. The low capacities of shallow reservoirs, where CO_2 would be in the gas phase, make them uneconomic because of storage inefficiency [3]. On the other hand, CO₂ storage in very deep reservoirs could also become highly uneconomic because of the high cost of well drilling and of CO₂ compression, and the low 'net' CO₂ storage (CO₂ sequestered minus CO₂ produced during





Figure 4: Pressure-Temperature phase diagram for CO₂ and three phases of CO₂⁽³⁰⁾.</sup>

compression). Thus, the pressure window of 9 MPa to 34.5 MPa is considered as being economic for CO₂ storage in depleted hydrocarbon reservoirs^[3], which roughly translates to a depth interval of 900 m to 3 500 m. In terms of CO₂ storage capacity, most reservoirs are relatively small in volume, and have a low capacity for CO₂ storage, rendering them uneconomic. On the other hand, associated oil and gas reservoirs (oil reservoirs with a gas cap) have a CO₂ storage capacity that is equal to the sum of the individual capacities of each reservoir. Considering the size of the major stationary CO₂ sources, it is most likely that only reservoirs with large CO₂ storage capacity would be considered in the short and medium terms. Building the infrastructure for CO₂ capture, transportation and injection is less costly if the size of the sink is large enough and if its lifespan is long enough to justify the needed investment and reduce the cost per ton of sequestered CO₂. Thus, only reservoirs with individual CO₂ storage capacity greater than 1 Mt CO₂ per year were selected at the end of the capacity assessment process.

Storage mechanisms of super-critical CO,

It weighs like a liquid and flows like a gas. The CO₂ would generally be injected underground as a so-called supercritical fluid. The somewhat alarming term 'super-critical' simply means that the CO₂ has a liquid-like density and flows like a gas, and with a decrease in pressure will expand to form a gas without a phase transition. The CO₂ density would still be less than water. The viscosity an inverse measure of how well the CO₂ flows would be typically less than a tenth of the brine resident in the rock. CO₂ cannot burn or explode; the only reaction that it can undergo in the subsurface is the precipitation of a solid. The injected CO₂ would migrate to the top of the rock layer because of buoyancy forces. Real interest is the long term of trapping the CO₂ for hundreds to thousands of years, it is imperative that the CO_2 could not escape. There are four principal ways in which the CO₂ is prevented from reaching the surface such as cap rock. Structural or stratigraphic trapping refers to low-permeability layers of rock (cap rock) that prevent the upwards movement of CO₂. Similar traps have held oil and gas underground for millions of years. The traps are comprised of salt, shale or clays: they need not be completely impermeable but have pore spaces that are so small that the CO₂ has insufficient pressure to enter. In well characterised formations, this is a good way to ensure storage. For instance, in Sleipner, the use of periodic seismic surveys (using sound waves to image the subsurface) have shown that the injected CO₂ rises to the top of the aquifer and then spreads out underneath low permeability cap rock layers at the top. However, if CCS is to be applied on a global scale, some storage sites may not be as well characterised as major oil and gas producing basins such as the North Sea. In this case another approach is required in case the cap rock contains gaps or fractures or is absent.

Dissolution

Over hundreds to thousands of years, the CO₂ would dissolve in the formation brine forming a denser phase that would sink. CO₂ at high pressure has a reasonably high solubility in water, although this solubility decreases as the brine becomes more saline, as an example, a 6 % sodium chloride solution almost twice as salty as sea water would dissolve approximately $30-40 \text{ kg/m}^3$ of CO₂ at temperatures of 80 °C and pressures of 10 MPa, representative of a reservoir at a depth of around 1 000 m where heat from the earth's core makes it hotter than near the surface. While this is promising, the dissolution of CO₂ is a slow process, mediated by molecular diffusion and the flow of the denser CO₂ laden brine. Simulation studies indicate that it takes hundreds to thousands of years for a significant fraction of the CO₂ to dissolve in typical reservoir settings [31, 32].

Reaction

The CO_2 dissolved in brine forms a weakly acidic solution that may react over thousands to millions of years with the host rock, forming solid carbonate. This is a complex geochemical process but in essence, oxides in the rock dissolve and then re-precipitate as carbonate. The opposite can also occur, in that the acidic brine dissolves part of the rock, increasing the volume of the pore space and the permeability. The speeds, extents and natures of these reactions depend principally on the mineralogy of the rock. Dissolution and precipitation both render the CO_2 less mobile over time. The storage security increases over hundreds to thousands of years. The problem is that these are slow processes: in the worst case, by the time a significant fraction of the CO_2 has dissolved, much of the CO_2 may already have escaped to the surface.

Capillary trapping

The final process, which is more rapid, is capillary trapping. This occurs when water displaces CO_2 in the pore space. Figure 5 shows this process coupled with dissolution at the field scale and illustrates CO_2 trapped at the pore scale.

Figure 5 shows the increasing storage effectiveness for CO₂ with depth and in the critical depth CO₂ is in gaseous state (balloons), below critical depth it is in liquid-like state (droplets). Volumetric relationship shown by blue numbers (e.g. 100 m^3 of CO₂ at surface would occupy 0.32 m³ at a depth of 1 km). Simulation studies of CO₂ storage have emphasised the importance of this mechanism. This process is well established in the oil industry. Water is used to displace oil from reservoirs but typically only around half the oil is recovered as much remains trapped in the pore space. Further water injection simply leads to excessive recycling of water from injection to the production wells with little or no further oil recovery this is why three barrels of water are recovered for every barrel of oil on average. The CO₂ would be trapped when it is displaced by water due to a

regional movement of groundwater or when a buoyant CO_2 plume migrates upwards. Recent work has suggested that pumping out saline water (brine) from the aquifer and then re-injecting would enhance this natural process, leading to the proposal of an injection scheme where CO_2 and brine are injected together followed by chase brine. The idea is to design injection so that all the CO_2 is trapped during the injection phase, making significant leakage very unlikely ^[31, 32].

Pressure responses

In the oil industry there is a net removal of fluid from the subsurface. The pressure in the reservoir drops and the rock, water and hydrocarbon expand to fill the space vacated by hydrocarbon. In most reservoirs, the natural expansion of rock and water surrounding the reservoir is insufficiently fast to prevent a very rapid drop in pressure. To compensate for this, to maintain pressure and push the oil out, water is usually injected hence the comments on water production in the preceding paragraph. In gas fields this is unnecessary, simply allowing the pressure to decrease allows the gas to expand and be produced. The obvious storage solution is to inject CO₂ to replace the oil and gas produced in old hydrocarbon fields. This has some advantages i.e. the field must have a good cap rock in order to contained the hydro-carbon for millions of years and so safe storage would be possible, the injection of CO₂ can enhance



Figure 5: Density of CO, versus ground depth and Different types of CO, trapping ^[12].

oil and gas production, giving some economic pay-back, next there is a pipeline infrastructure in place for injection. The injected CO₂ would cause the reservoir pressure to rise again, replacing the volume of produced hydrocarbons. The main disadvantage is that the extra production causes more CO₂ to be burnt when extra oil and gas is produced typically at least as much CO_2 as is stored. The CO_2 displaces brine and the increased fluid pressure tends to expand the pore space, pushing the rock apart. If the fluid pressure is too high, this can fracture the rock, creating cracks through which the CO₂ could escape. This squeezing of the subsurface also leads to regional pressure increases, which again could cause extensive fracturing, or the seepage of salty water to displace fresh water, contaminating drinking water supplies. The experience of Sleipner and other sites where large volumes of CO₂ have been injected without significant increases in pressure provides evidence that large aquifers do have substantial storage capacities. Some indications have shown there are huge volumes in which the pressure can be dissipated. In reality the amount of CO₂ that can be stored is a function of how the injection is engineered, how many wells are drilled, what sort of wells and whether or not brine is produced. The storage design depends on economics and the field properties, and so it is usually unrealistic to talk of a single capacity estimate.

Dynamic capacity

The first consideration is injectivity, or dynamic storage capacity. This means, can the CO_2 be injected at the rate required in the single well. The use of additional wells or horizontal wells through layers of high permeability come with an additional cost but would allow CO_2 to be injected more rapidly ^[33]. Current field experience indicates that a single well can readily inject up to 1 Mt of CO_2 per year but more than one injection well would therefore be required for large storage projects, especially if CO_2 is collected from several sources before injection.

Static capacity

Large, regionally-extensive aquifers almost certainly have sufficient storage capacity even under rather modest constraints on pressure increase. The second concern is the extent of the CO₂ itself, since this indicates the potential footprint for any escape. Simulation studies suggest than in highly heterogeneous systems, the lowest storage capacity is around 2 % of the pore space. As the pore space itself is around 25 % of the rock volume, this represents around 0.5 % of the total rock volume, which is similar to the capacity estimated using pressure constraints. The storage capacity and storage security could be improved, through improved injection design. If it is known that there is a good cap rock (such as in hydrocarbon reservoirs), CO₂ could be allowed to accumulate under the cap rock, where it could occupy the majority of the pore space. In the oil industry, it is standard practice to inject gas and water together or in alternating slugs, as the mobility of the combination of the two phases has a lower mobility than CO₂ alone, leading to a more stable displacement and a more efficient sweep of the reservoir. In contrast, CO_2 alone has a very high mobility (low viscosity) and tends to rise to the top of the reservoir and channel along high permeability channels. The results of a simulation study on a North Sea aquifer indicated that, with only a short period of brine injection, the vast majority of the CO₂ could be capillary trapped, ensuring permanent storage ^[11, 34]. It is never possible to guarantee that a cap rock will be impermeable to CO₂, or that the permeability would be sufficiently high to allow rapid injection. Compressibility is defined as the fractional change in volume for a unit increase in pressure. When CO₂ is injected at high pressure, it compresses the resident brine and pushes the rock apart, increasing the pore volume. The combination of rock and brine has a compressibility of around 10⁻⁹ Pa⁻¹. An aquifer at a depth of 1 000 m would typically have a pressure of around 10 MPa to avoid fracturing it would be wise to limit the pressure increase to between 10 % and 50 %. Hence the pressure should increase by no more than 1 MPa to 5 MPa. This leads to a fractional change in volume of the order $1-5 \times 10^{-3}$ or 0.1-0.5 % a regionally extensive aquifer some 100 km long and 100 km wide with permeable layers of a total thickness of 1 km has a total rock volume of the order of 10⁴ km³ or 10¹³ m³. Using typical density of 600 kg/m^3 , this would allow the
storage of 6 Gt to 30 Gt of CO_2 but application of CCS at a global scale for several decades; it would still need to store CO_2 in many large aquifer units around the world.

Temporary CO₂ storage in existing or new underground caverns

Temporary storage of CO₂ in underground facilities requires detailed analysis of all influencing factors, which include in addition to the geological structure of the area and engineering geological, hydrogeological and geotechnical evaluation includes depth below the ground surface and not least information about the inhabited environment. Temporary storage of CO_2 has a practical goal in the case finding out a location of proper sound rock mass between the place of CO₂ capture and the compressed and final storage phases. In Figure 6 the proposed location of temporary storage is possible between the previous mentioned primary and final technological procedure of long term storage of CO₂.

For such storage the specific conditions laid down by the goal of optimal CO_2 pressure and temperature should be taken into account to achieve the appropriate density during its storage. Based on the phase diagram of CO_2 (Figure 4) the gas pressure has to be calculated from 80 bar to 90 bar at temperatures between 10 °C and 15 °C ^[35]. In practice there may be other combinations of temperature and pressure which depend of the natural conditions of a potential storage area. In these decisions, it is necessary to have sufficient reliable data of the rock environment including projected depth of



Figure 6: A Schematic Illustrating Carbon Dioxide Capture and Storage (© British Geological Survey)^[12].

storage, natural rocks temperature, and finally information about possible seismic activity.

Existing types of underground caverns

Man-made cavities

Great Britain has a very long history of mining and there are very few minerals that have not been worked underground at some stage in the past. Coal mining was by far the most extensive but metal mining formerly also covered large areas. However, many other minerals, including oil shale, fireclay, ball clay, fuller's earth, limestone, building stone, silica sand, fluorspar, barytes, slate and, notably the evaporate minerals salt, gypsum/anhydrite and potash have all been mined to a greater or lesser extent. All these activities have created underground caverns of varying sizes and shapes over a wide range of geological settings. For most minerals this has produced voids, which are unstable, particularly where early mining methods were employed ^[36]. The type of void created and its suitability for storage use depends on the rock worked and the type of mining method used. Modern room and pillar mining is used for generally flat-lying, sedimentary strata. Typically 25–50 % of the rock is left in the form of square pillars to provide a permanent support for the roof. Rock salt mining is a good example. Modern salt solution mining techniques also have the capacity to produce stable cavities ideally suited for certain types of storage.

Salt caverns and abandoned coal mines

Salt occurs in nature either in solid form as rock salt (halite) in beds ranging from a few centimetres to hundreds of meters thick, or in solution as brine. Salt caverns are constructed in naturally occurring thick salt domes, deep underground. Salt can be found in almost every part of the world with some exceptions around the Pacific Rim. Salt caverns are a proven medium for hydro-carbon storage as salt acts as a natural sealant, trapping the natural gas inside the cavern. Salt caverns for gas storage use are formed with a leaching process by pumping hot water to dissolve the salt and removing the resulting brine via a single well, which then serves for gas injection and withdrawal. The storage capacity for a given cavity volume (several hundreds of thousands to several million cubic metres) is proportional to the maximum operating pressure, which depends on the depth. Salt caverns are typically much smaller than depleted gas reservoirs and aquifers, usually covering only one-hundredth of the acreage taken up by a depleted gas reservoir. As such, they are particularly suited for short-term storage of natural gas because of their high deliverability as well as the ability to quickly switch from injection to withdrawal. As with depleted gas reservoirs and salt caverns, CO₂ stored in coal mines is inspired by storage projects for natural gas in abandoned coal mines, the oldest of which dates back to 1961. One of the typical cases is the Levden coal mines. located near Denver Colorado, which were in operation from 1903 until 1950, producing 5.4 Mt sub-bituminous coals from two horizontal seams at 210 m and 225 m depth in the upper Cretaceous Laramin formation. The second case is two abandoned mines converted into natural gas storage reservoirs, both located in the gassy Hainaut coalfield in southern Belgium^[23, 37]. Experts carried out a detailed feasibility study on using abandoned coal mines for long-term CO_2 , storage, with special reference to a Belgian colliery. CO₂ stored in an abandoned coal mine may exist in the gas phase, in solution in water and adsorbed on remaining coal. The storage capacity has been estimated at between 7.5 Mt to 12.5 Mt CO₂, which maybe small but accounts for approximately 3 % to 6 % of the emission reduction for Belgium required under the Kyoto agreement. The technical set-up of an abandoned coal mine storage project is relatively simple. Unlike unminable coal seams, CO₂ induced swelling is not an issue here. In fact, the seams surrounding former mine workings are naturally stimulated and thus high injection rates can be achieved. On the other hand, fractured rock which exists around an abandoned coal mine may provide leakage paths for CO₂ which would be unacceptable for a storage site ^[23, 37]. The same authors have suggested some special requirements which need to be met in order to obtain a safe and stable reservoir with sufficient capacity. Firstly, the highest level of the mine should be at least 500 m deep, with well-sealed shafts and a tight, mostly dry cap rock. Secondly, in order to pre-

vent mine flooding, the storage pressure should be higher than the hydrostatic pressure of the surrounding strata. This overpressure, typically around 130 % of the hydrostatic pressure, in turn places a stringent leak-proof requirement on the top seal of the reservoir and the existing shafts.

Existing underground caverns used for different storages

In some places around the world you can find many underground caverns over the last six decades. Some of them were done connected to military activities, defence regulations and many other requests in the goal to improve conditions for storage energetic, water and air masses. Big advantages were done in Norway, where all the mentioned time has clearer strategy in which way can underground available space been used. In the scientific and technical literature can found many usable technical solutions including geological and geotechnical assessments of hoisted rock masses in the goal to find proper economic and environmental acceptation. It is not unknown, that natural physical, chemical and geotechnical characteristics of rocks mass in these cases have played enormous important game because the hoisted media has more than one influence on the potential used of available underground space. In the next chapter high attention will be paid to Norwegian and other Scandinavian experiences [9, 36-38].

Self-standing capacity

Most rock mass have a certain self-supporting capacity, although this capacity may vary within a wide range. An appropriate engineering approach is to take this capacity into account when designing permanent support. As for any type of underground structures the selection of the site location, orientation and shape of the caverns are important steps preceding the dimensioning and the laying out of the underground site. Rock strengthening may, however be needed to secure certain properties/ specified capacities, the same way as is the case for any other construction material. The fact that, the rock mass is not a homogenous material should not disgualify the utilisation of its self-standing and load bearing capacity. Typically, rock support application in Norwegian oil and gas storage facilities consists mainly of rock bolting and spraved concrete. The application of cast-in-place concrete lining in such facilities has been limited to concrete plugs and similar structures and is normally not applied for rock support purposes. The rock support measures are typically not considered as contributing to the containment, other than indirectly by securing the rock contour and thus preventing it from loosening. Furthermore, the Norwegian tunnelling concept applies widely as a drained concept, meaning that the rock support structure is drained and the water is collected and lead to the drainage system. Thus the rock support is not designed to withstand the full hydrostatic pressure in the rock mass because the self-load-bearing capacity was applied in the design process. The experience with large underground caverns was obtained in Norway during the development of hydroelectric power schemes for which purpose a total of 200 underground plants were constructed. Commonly the caverns for power-houses and hydrocarbon storage were all typically sized to some 15-20 m width, 20-30 m height and tens-hundreds meter length. That geometrical data, based on past experiences can be usable for CO₂ storage systems. Various types of monitoring to follow-up the behaviour of the rock mass and the support structures are available and used to document the stability and behaviour of the rock mass [38-40].

Identification of design parameters

The locations of the rock caverns are normally fixed within the design concept and being based on information gathered during a comprehensive pre-investigation phase, however, depending on the actual rock mass conditions as encountered during tunnelling in the approach to the designed and planned location, relocation of the underground structure may of course take place. Several underground projects in Norway have experienced changed locations and local optimisation to better adapt to the actual rock mass conditions. It is common to take into account the next information relating to:

- rock types and mechanical properties
- characteristics and frequency, spacing of rock mass discontinuities
- in-situ rock stresses
- groundwater conditions.

During the approach to the planned location of the cavern(s) the rock mass is thoroughly mapped, joint systems are observed and characterised, weakness zones are interpreted, in-situ rock stresses are measured, ground water is monitored (Figure 7). If these conditions are not in accordance with the expected and required quality of the rock mass, it may be conclusively decided to shift the location of the storage caverns to other adjacent caverns and tunnels, or make some layout adjustments. Typically, the final layouts of the caverns, their locations, geometries, alignments, lay-outs of the tunnel system and rock support design may not be finally decided upon until the above information is obtained from the excavation of the approaches of access tunnels. Numerical analyses as well as analytical calculations are useful tools for the designing and planning of the caverns. These must of course be verified during the construction phase by adequate monitoring and follow-up of the stability of the underground caverns.



Figure 7: Underground cavern under construction [36].

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Assessment of the CO₂ pressure impact of on the walls of caverns

The statically base of the CO₂ pressure acting on the caverns' walls we can apply for calculating stress and strain relationships in the lining and surrounding rock structure. According to the strain nonlinear softening constitutive model of practical rock, the pressure tunnel with liner is analysed. The model is considers the influence of intermediate principal stress σ_2 . Stress distribution laws of surrounding rock plastic zone of tunnel, the mechanism of load bearing and acting relationship between surrounding rock and support are studied. Some important concepts of the working status of practical tunnel surrounding rock are obtained: such a superior certain limit $[S_{\max}]$ of self-support geostress and inferior certain limit $[S_{min}]$ of support less tunnel surrounding rock. The relations between $[S_{max}]$ and geo-stress, between $[S_{min}]$ and geo-stress are given. Calculation shows that the assumed model agrees well with practical conditions of the rocks. Analysis shows that the ideal plastic model and the brittle model are special cases of the proposed solution.

It is well known that the stability of tunnel surrounding rock is decided by the interaction results of stresses in the surrounding rock and its strength, i.e. surrounding rock states. If its surrounding rock is in elastic or plastic state after a tunnel is driven, the surrounding rock is stable. However, if its surrounding rock is in a broken state after the tunnel is driven, the surrounding rock is unstable. In addition, lots of in-situ observation data have shown that a broken zone exists widely in surrounding rocks of tunnels. Therefore, it can be seen that the thickness of the broken zone, a geometrical parameter indicating the broken range in the surrounding rocks of tunnels, can be taken as a comprehensive index of stresses in the surrounding rock and its strength to evaluate the stability of surrounding rock of a deep tunnel. Kastner's solution is often used in elastic-plastic analysis for surrounding rock of a circular tunnel. It is well known that Kastner's formula is based on an ideal elastic-plastic model. This leads to the Kastner's solution and is far away from corresponding actual values in surrounding rock. Following along the path pioneered by Kastner, researchers have published different solutions for surrounding rocks of circular tunnels ^[41]. However, these solutions are restricted to very simple material models, such as the simple linear relationship between stress-strain.

Numerical analysis used BEM- EXAMINE 2D

For preliminary analysis the stability assessment of unlined rock caverns in more stages without and with CO₂ pressure, the 2D modelling was used ^[42]. The main advantages of the presented modelling were in the parametrical analysis which shows what influences of each of them on stability are present. Using BEM to determine the strength factor of the host rock mass the calculations were done in the cases when the caverns with dimensions W/H 21 m/31 m were empty and in the case where CO₂ was filled with 8 MPa pressure (Figure 8). Technology of CO₂ pumping in to the caverns in the analysis are not included in detail because in the presented type of preliminary analysis is unnecessary. The important question is the factor of safety of the cavern's stability explains the real situation enough as to which can be present in the underground environment. Results of calculations, which are shown below, clearly explain that the influence of CO₂ pressure 8 MPa on the unlined rock cavern wall is very high. At the same case it is clear that the depth of the cavern location below ground surface has an important influence on stability, too. The results of calculation shows that in the proposed geometry of an underground unlined cavern with no loaded and loaded with CO₂ inner pressure $P_2 = 8$ MPa, the host rock would not have enough strength in practically all calculated cases. The geotechnical characteristics of the host rock which were used in the present calculations are the same as used in the paper Thermal Behaviour of Rock in Relation to Underground Gas Storage, prepared by Ming Lu (2007) [43].

- Horizontal stress ratio = 1.5
- Out of plane stress ratio = 1.7
- E-modulus = 30 GPa
- Poisson's ratio= 0.28
 - Friction angle = 38°

- Cohesion = 0.5 MPa

– Tensile strength = 0.7 MPa

- Unit weight = 27 kN/m^3 .

For detailed analysis of the geotechnical stability of the virtual temporary CO_2 storage another geotechnical parameters can be used. It's no doubt, that in previous experience in underground big caverns construction in better rock mass conditions, the stability analysis should not be a part of the problem. Short looking through geological environments which are possible locations of the future CO_2 storages gave optimistic plans for underground space used for such types of projects.

The caverns stability analysis was given in the comparison of calculated strength factors (FS) for different load and geometric cases. In the next figures the results of calculations are shown in the name of the Strength factor, as results of the mentioned analysis. In the first case only one cavern was analysed. First analysis of the single unlined cavern stability was done for empty available volume space (Figure 8) and the cavern filled with CO_2 (Figure 9). In the figures the geometry of the proposed cavern is shown, too. The dimensions which are included in the analysis are close to that used in construction practice in Norway.

Based on previous research of primary stress states at different locations, the coefficient of primary stress ratio 1.5 is accepted. In Figures 8, 9, 10, 11 and 12 where the results of 2D numerical modelling are shown, it can found that the cavern in the proposed rock mass environment is unstable without installation of the support system. The greater differences exist between the depths 100 m, 200 m and 300 m but deeper location i.e. 400 m has no important influence on the calculated strength factors. They are similar to the factors, which were found for the case where the virtual cavern was at the 300 m depth. In a similar way the 2D analysis was done for a single cavern filled with CO₂ under 8 MPa pressure. Geometrical and loading position and the results of analyses for four different location depths it can be found in Figure 11. The results, which are shown in Figure 11, were not looked at as surprising regarding those given in the input data. They are understandable, as the pressure of CO_2 in this case even improved the stability of the cavern.

The case where two caverns are located 58 m between axis shows that that the unlined caverns are unstable without some support measures. The stress influence between caverns is higher in the greater depths. That is easily understandable because the coefficient of primary stress state is 1.5 which means that in such primary conditions the axes distance should be longer. Calculated SF for the unlined caverns where only left loaded with CO₂ pressure at different depths. Interesting results are shown in Figure 11 where the effect of CO₂ pressure on the temporary stability of the left cavern is evident. The main positive influence on stability is present at the depths below the 100 m for both cases presented in Figure 11 and Figure 12. The presented results of 2D calculations are informative. The purpose of this numerical analysis was to show some limitations which are necessary when planning or updating existing underground caverns, which were probably used for temporary storage of CO₂. Indeed, the geotechnical input parameters that were considered in this analysis took the pessimistic values, so that it is possible with a greater degree of optimism to look at more favourable rock mass circumstances. For further activities in this field of underground space used, detailed plan for the necessary in-depth research and analysis of real sites, which are potential sites in the future, would be needed.



Figure 8: Geometry of single cavern with no loading with CO_2 pressure and calculated FS for different depths of cavern positions.



Figure 9: Geometry of the single cavern for CO₂ storage with pressure 8 MPa and calculated FS for a single unlined cavern located at different depths.



Figure 10: Two unlined caverns not loading with CO₂ pressure and calculated SF for different depths below the surface.



Figure 11: Layout of two unlined caverns, left filled with CO_2 with 8 MPa working pressure, right with no inside pressure and calculated SFs for different depths.



Figure 12: Layouts of two caverns filled with CO₂ under working pressure 8 MPa. Calculated Strength factors for the unlined two caverns, loaded with 8 MPa CO₂ pressure at different depths.

Specific requirements for lining caverns for providing storage of CO_2

If the CO₂ pressure has over 100 bar, when the cavern is closed and the surrounding rocks have temperature around 10 °C, the big advantage would not achieved. The main reason is when the pressure of CO_2 is lower than 45 bar it will act as a gas (gas law for real gases). When the temperature of the CO_2 is the same as the temperature of surroundings rocks i.e. approx. 10 °C, the equilibrium pressure between liquid and gas is 45 bar. If CO₂ continues to be pumped into the cavern, the gas will follow the characteristics which are adequate to fluid and will still continue volume of fluid increases. The volume of gas above the liquid CO₂ is less until the cavern full of liquid CO₂, but the pressure is still 45 bar. If CO₂ pressure is slowly increased with additional pumping, say from 45 bar to 150 bar, liquid CO2 is indeed a bit compressed, but the compressibility of fluid is very small, so the pressure increase from 45 bar to 150 bar gain just fluid volume ^[26, 35]. In the case that the higher pressure CO₂ by the offline, faster pumping gas into the cavern, the balance is not changed. At the beginning CO₂ pressure is of course somewhat higher but when the gas is cooled to 10 °C, the equilibrium pressure would be 45 bar. Of course, it may take several days / weeks / months for the surrounding rock environment and CO₂ in the caverns to reach equilibrium. At the beginning, when the

pumping gas is warm (25 °C), the pressure above 45 bar may even have 100 bar or high value. When the surroundings cool; more and more the pressure would decrease and in the end, if time allows, would stabilise at 45 bar (if there is already some liquid).The density of liquid at 10 °C should be somewhere around 0.45 kg/l, at the critical temperature it was 0.47 kg/l. The problem could arise if CO_2 were to be warmed at the critical temperature i.e. 31 °C. In that case the CO_2 would be changed to gas which causes increasing pressure because it would behave as a gas and no longer a liquid.

Conclusions

The underground storage of industrial quantities of carbon dioxide is technically possible, and CO_2 storage both in saline water-filled reservoir rocks and in oil and gas fields has reached the demonstration stage. Nonetheless, the indications are that underground CO_2 storage could have a significant impact on our greenhouse gas emissions.

Underground storage may involve substantial construction work, including major surface infrastructure provision (access roads, rail links, pipelines, head works buildings) and not just restricted to the immediate locality. All of these may create more or new impacts in terms of amenities and traffic. Offshore storage may require new or expanded onshore installations and infrastructure. Concerns in relation to stability, pollution and safety would also need to be addressed.

In some situations underground storage can be considered as a three stage activity; a shortterm development stage (the 'temporary' work involved in construction of the void and the associated surface works including infrastructure); a long-term operational stage (the permanent use of the resulting void); and finally a decommissioning and post abandonment stage (when the planning impacts arising from the presence of the facility and the infrastructure may need relevant considerations for a considerable period of time.

Storage of CO_2 underground could reduce construction costs and offer protection from storms, accidents, arson, acts of terrorism and

also prevent 'shrinkage' (loss by theft). It may also provide an ideal ambient environment in terms of stable humidity and temperature and be dry, reducing energy costs for heating or air conditioning. However, some storage facilities may be wet, hot or very dry with issues of air quality inhibiting access and might raise concerns about managing fire or pollution events. Ventilation, access and fire escape structures may be required at the surface. Surface stability would also be a major planning consideration.

Experience with the use of water curtains at the three Norwegian air storages discussed herein, at pressures from 4 MPa to 8 MPa, is encouraging. It has been found that a properly designed water curtain totally eliminates any gas leakage from the storage, even for a storage pressure head that is only twice the thickness of the rock overburden. A water curtain may provide not only a cost-effective method for restricting gas leakage from unlined hard rock caverns; currently it also appears to be the only practical way of totally preventing gas leakage from high pressure storage.

The main advantages of CO_2 underground storage in rock mass formation are very wide including utilising rock mass properties, environmentally-friendly, protection during wartime, operation and maintenance, and not least protection from natural catastrophes.

The rock mass has a number of important parameters that are utilised in the underground storage of hydrocarbon products. These capacities allow a variety of storage conditions and enable a number of diverse types of products to be stored in unlined rock caverns.

With the current knowledge of the mechanical and thermodynamic behaviour of the rock mass and the current use of such storage facilities the proven technologies could take place during the construction process.

As far as the environmental aspects are concerned the experience from Norwegian underground storage projects are unreservedly positive. So far product leakages have not been reported at any of these projects indicating clearly that the applied concept and techniques for obtaining the required confinement are appropriately proven.

For a subsurface solution, dedicated systems for collection and handling of various types of

spill could be planned thus limiting the spread of any spill. Bringing these storage tanks below the surface allows valuable surface areas to be utilised for other purposes; recreational, cultural and residential. In addition unsightly structures can be hidden away underground. Protection from natural disasters and catastro-

phes such as earthquakes is a beneficial advantage of underground storage. It has been acknowledged that subsurface structures have several intrinsic advantages in resisting earthquake motions. Experience and calculations show this clearly.

The total construction cost would be within the range of 150–310 USD per m³ storage which would be many times competitive in the open construction market.

For any decision about working pressure and temperature of CO_2 a phase diagram should be used regarding the names and technological possibilities. Two potential solutions exist; first include pressure 80 bar to 100 bar at the normal rock temperature 8 °C to 12 °C. In this case additional isolation and a freezing system aren't needed. The second case is close to CO_2 transport parameters at pressure of about 7 bar and temperature –50 °C. The final decision depends of the financial and technological closed cycle of the CO_2 long-term storage.

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Determining compatness of the quality of natural stone blocks with ultrasonic technic

Določanje kompaktnosti blokov naravnega kamna z ultrazvokom

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Abstract

The company Marmor Sežana d. d., has been engaged in the excavation, processing and installation of natural stone - limestone in Slovenia and worldwide since 1947. Natural stone is produced in our quarries. Natural stone is a specific type of mineral raw material, produced in large blocks, parallelepiped shaped monoliths. An important specificity of extracting natural stone is the requirement for compactness. In Slovenia, where tectonics is strongly expressed, it is difficult to ensure compactness. Furthermore, the extraction is hampered by the increasing demand for large dimensions of natural stone blocks. Irregularities in blocks and thereby the quality has so far been determined only visually; pouring water on the block and inspecting it visually, and by banging on the block and listening to the echoes. Recently, the demands about the quality of the blocks have surfaced, as the producers are eager to ensure the best possible utilization of the material depending on the desired end product and to reduce the backlog in production processes. For this reason, only a visual inspection of the blocks is no longer sufficient.

Key words: ultrasonic examinations, natural stone, geological research

Izvleček

Družba Marmor, Sežana d. d., se že od leta 1947 ukvarja s pridobivanjem, obdelavo in vgradnjo naravnega kamna - apnenca pri nas in po celem svetu. Naravni kamen pridobivamo v svojih kamnolomih. Naravni kamen je specifična vrsta mineralne surovine, ki se pridobiva v čim večjih blokih, monolitih paralelepipedne oblike. Pomembna specifičnost pridobivanja naravnega kamna je zahteva po kompaktnosti. V Sloveniji, kjer je tektonika močno izražena, je kompaktnost težko zagotoviti. Dodatno pridobivanje otežuje tudi vedno večje povpraševanje po velikih gabaritih blokov naravnega kamna. Nepravilnosti v blokih in s tem kvaliteta so se do sedaj določale le vizualno; s polivanjem bloka z vodo in vizualnega pregleda ter z udarjanjem po bloku in poslušanjem odmeva. Na trgu se v zadnjem času pojavljajo zahteve o garanciji kvalitete prodanih blokov. Investitorji si na ta način želijo zagotoviti čim boljšo izrabo materiala glede na želene končne produkte. Zaradi tega samo vizualni pregled blokov ne zadošča več.

Ključne besede: ultrazvočne preiskave, naravni kamen, geološke raziskave

Introduction

According to past experience, the greatest difficulty in extracting natural stone are the consequences of tectonics, especially cracks and fragmentation (Vesel, 1975). Due to increasing demands for large dimensions of natural stone blocks, the knowledge about the content of the irregularities in the blocks is very important. Quality of the blocks or monoliths has so far been determined only visually, that is by pouring water on the block and inspecting it visually, and by banging on the block and listening to the echoes. The course of the irregularities (cracks) can thus be determined only superficially, however, we cannot predict how deep they actually are. Sometimes a crack occurs just a few centimeters below the surface of the block and intersects the majority of the block, but cannot be detected on the surface. This often leads to complaints or can even damage the processing machines. The demands of investors for larger slabs and for optimizing the utilization of the block, lead to the fact, that it is necessary to assess the natural stone block not only visually, but also to determine its internal structure. A more detailed inspection and determination of quality enables more rational and economical use of the material, as mistakes about cutting are often made during the preparation and processing of the block. The internal structure of the block can be determined by using ultrasonic methods. Ultrasonic devices are used for determination of defects, voids, cracks, etc. in situ in the concrete constructions, which gives us information about the homogeneity of the material. In practice, a speed measurement profile can help assesss the degree of homogeneity of a natural stone block.

Currently, we performs ultrasonic measurements of natural stone blocks in predefined profiles, on which the travel speed of waves is measured. Speed measurements of travelling waves with ultrasonic instrument and with it the determination of quality of natural stone blocks will be implemented on a limestone of the Upper Cretaceous age, known under trade names Lipica enotni, Lipica rožasti, Koprivo and Repen. Our goal is to create the categorization of natural stone bloks quality on the basis of statistical processing of a large number of measurement data. The current classification is based solely on visual inspection of each block of limestone and its dimensions, but gives no information on the internal compactness of the block. The task is also to remove damaged, cracked, and poor quality parts of the block and combine them into a larger composit block by using the polyester resin, and later on cut it on the gangsaw.

Ultrasonic examinations of natural stone

Ultrasonic devices have been in use since before the Second World War. Sound waves and echoes were used to help detect icebergs, search for sunken submarines and measure sea depth on the basis of the reflected waves. In 1929 Sokoloff proposed detecting faults in the material by using ultrasound and in 1934 he conducted the first practical experiments with ultrasonic control on metal objects. In 1931 Mulhauser patented the use of control by ultrasound and determining the relationships in the material and errors in it. Firestone (1942) patented the first impulse reverberation instrument. The terminology of »ultrasound« means high-frequency waves, which are frequencies higher than human hearing (Meola, Maio, Roberti, Carlomagno; Bray, et.al, 1992). Ultrasonic devices are now portable to allow for the implementation of in situ researches, making them less expensive. Ultrasonic examinations are useful techniques, especially when researching properties of stone such as elasticity, anisotropy, mechanical strength and condition of deterioration (Christaras, 1999). The techniques enable an assessment in relation to the sound of the stone, with which we can identify the authenticity of discontinuities or defects in materials, such as demolishing zones and voids (Bray, et al 1992: 278, Kahraman, et al., 2008). They are also useful in tracking and studying changes in basic physical and mechanical properties of stone in relation to moisture, weathering and stress (Christaras, 1999; Kahraman, et. al. 2008). The methods, where we discover irregularities in the material structure, dimensions, physical and mechanical properties, chemical analysis and voltage without damaging the material,

are called non-destructive methods (NDT) and have been in use for several decades. The aim was to detect cracks and irregularities in the material in a way, that does not further damages the material and that causes no additional damage to the cracks during the investigation (Akveren 2010). Non-destructive methods are mainly used in mechanical engineering (control of steel wires, metal elements), in construction for concrete control (Trtnik, 2012), in examinations of stone elements, electrical engineering, medicine, arts, forensics. (Bodare, 2005).

Measurement techniques using ultrasonic technic on natural stone

Acoustic methods are based on generating, disseminating and reflecting mechanical sound waves in solids, where the latter depends on the density and elastic properties of the used material, the frequency of waves, and on the method of generating and receiving sound waves (Špeglič, 2013). Transmitters and receivers are piezoelectric devices that transmit and receive waves. Ultrasonic frequencies are frequencies above 20 kHz (Wiberg, 1994). Ultrasonic methods are based on the passage and reflection of ultrasonic waves, generated by transmitter and detected by receiver. Transmitters generate longitudinal, transverse waves, which spread depending on the mechanical properties of the material. Measurements of the material, through which ultrasonic impulse velocity passes, can be made in three ways: direct, semi-direct and indirect (Kahrman, et al., 2008, Meola, et al., 2005). For quality measurements the surface of the material being measured should be smooth, so that transmitters and receivers have a good contact. To ensure a good contact a gel can also be used (Meola, e soil. 2005). According to the authors Lemona and Christaras (1999), a direct method is the most satisfactory method, where the direction of waves is parallel to the transducers. If the transducers are on the opposite side of the material, the spread of the impulses will be faster and pulse velocity larger than in the indirect method. The indirect method is used for finding the depth of weathering, degree of consolidation and to detect cracks near the surface (Lemon and Christaras, 1999, Akveren 2010).



Figure 1: Ultrasound instrument Boviar with ultrasound probe and a hammer.

Transmitter:	
Frequency	55 kHz
Voltage	1,6 kV
Energy	0,05 J
Weight	770 g
Dimension	50 mm × 75 mm
Receiver:	
Frequency Range	1 - 70kHz
Sensitivity	1 kHz = 4 840 mV/g
Top Sensitivity	6 kHz = 30 V/g
pre-amplified Receiver	20 dB
Weight	760 g
Dimension	50 mm × 75 mm

Hammer-transmitter, with which the system is equiped, is intended for use when energy of piezoelectric transmitters TSG-55 and TSG-Hi20 is not sufficient for the examination. In such circumstances the received signal is too weak and can not be properly analyzed or it is difficult to determine the first arrival of the signal (First Break Pick). Signal by means of hammer is characterized by low frequency and high energy consumption. The device is used for a material with outstanding low wave propagation characteristics or for a material of large dimensions.

There are some known examples of ultrasound examinations from the past, for example on architectural ornamental stone in the case of reconstruction of stone elements, or examination of stone monuments and decorative panels, on which the irregularities as a result of weathering or due to inadequate installation technology were observed.

Ultrasonic measurements on natural stone blocks

Since the deposits of natural stone in the Karst (Slovenia) are subject to strong local tectonics, they generally contain a lot of interruption surfaces. This is also reflected in compactnes and maximum dimensions of the blocks, which include a number of irregularities. For a proper classification of blocks regarding the quality of both external surfaces and interior of the blocks, we carried out several in-situ measurements and then compared the data with the actual state of the panels that were gained by sawing the blocks. Doing so we obtained the first information that give us a rough estimate on the applicability of the method, however, in order to make the categorization, more measurements need to be performed and more data, that will be statistically representative, need to be obtained.

Measurements of the speed of ultrasonic waves passing through the material were carried out on the sample. We used a pulsed ultrasound at a frequency of 55 kHz. The sound that arises from the piezoelectric transducer does not originate from a point, but from practically the entire surface of the element. Round converters are sometimes also called cylinder sources, as the sound in front of transmiter expands in the shape of a cylinder. (Medvešček). According to the scientific literature and practical experience the rule applies, that the defects in the material which are larger than ½ of wavelength can be detected. Resolution and sensitivity are also important for detecting defects.

Sensitivity is the ability to detect small defects and usually increases with increasing the frequency (decrease in wavelength). Resolution is the ability of the system to detect errors that are packed closely together in the material or that are in the vicinity of the surface. Resolution also increases with the frequency.

By increasing the frequency the opposite effect can also be achieved. If our observed material is not completely homogeneous, we will get reflections at high frequencies due to grain size of the material and the microscopic irregularities. In this way the maximum depth that can be achieved will be reduced, because as a result of reflection the wave power declines rapidly. (Medvešček).

The first part of the research was carried out in the laboratory on previously selected samples, where we sought to discover differences in sound pressure measurement with a pulse unit. The results are shown in the Table 2.

To perform in situ measurements we used the Boviar instrument and a computer program DataSonic by Boviar S.r.l. company. The program calculates on the basis of measurements that are conducted with the help of the following equation.

Among the most important characteristics of sound are speed *c*, frequency *f* and wavelength λ . Wavelength is proportional to the speed



Figure 2: Opening of slabs on a gangsaw.



Material	cp (m/s)	cS (m/s)	αP 105 (1/m)	Q
Granite	5000-6000	2500-3300	0.21-0.38	9800-15000
Granodiorite	4780	3100		
Diorite	5780	3060	0.21	12900
Gabbro	6450	3420		
Basalt	5400-6400	2700-3500	0.41(5500)	6900
Dunite	6800-8640	3500-4400		
Gniess	3500-7500			
Marble	3700-7000			
Sandstone	1400-4300		0.71(4300)-1.77(4000)	2200-5100
Limestone	5900-6100	2800-3100	0.37 (6000)	7100
Anhydrite	4100			
Shale	2100-3400		0.68(3300) - 2.32(2150)	3100-7100

Table 1: Transitions of transverse and shear waves through certain stones by Dobrin (1976). a- value is set to 50 Hz frequency. a- and Q values are shown in the table below

of the wave and inversely proportional to the frequency, as shown in the following equation

$$\lambda = \frac{c}{f} \tag{1}$$

The speed of passage of ultrasonic waves (c_i) from the transmitter to the receiver is calculated according to the equation, l is the length of the measured profile and t is the time of passage of longitudinal waves

$$c_i = \frac{l}{t} \left(\frac{km}{s}\right) \tag{2}$$

With the help of a large number of measurements, we have calculated the mean value that will determine the quality of the block

$$\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i = \frac{1}{n} \cdot (x_1 + \dots + x_n)$$
(3)

The standard deviation can be calculated as σ (sigma), that is as a deviation of the total population or its random variable, or as *s*, that is as deviation of each sample of the statistical population. The formulas for the two deviations differ.

$$\bar{s}_{x} = \sqrt{\frac{\sum_{i=1}^{N} (x_{i} - \bar{x})^{2}}{N - 1}}$$
(4)

where x_i is the i-th unit in the statistical population, the arithmetic mean of the population and N is the number of all units



Figure 3: Setting up profiles of ultrasonic measurement on natural stone block.

The measurements were carried out on blocks of large dimensions. Thus, we tested the real possibility of using this method on blocks of natural stone - limestone. The figure below shows the placement of measuring profiles on a glued block and an overview of obtained panels, as well as a comparison with the results of measurements on the block from which the panels were cut.



Figure 4: Display of measurements on the laboratory specimen. An example of a crack in the middle of the block (a) and the measured velocity of ultrasonic waves of 3.98 km/s (b).

Profiles for measuring the block were determined by width in three lines, namely at 1/6 of the distance of width and height; lengthwise in two lines at an interval of 1/6 of the length, and heightwise in two lines at an interval of 1/3 of the height. Density of the profiles depends on the dimensions of the blocks and on the results of the measurements. In the event that there are significant deviations, the profiles must be condensed. On the basis of the profiles' density, it is possible to follow a crack, which is located in the block. Block in Figure 5 was characterized by an average speed of sound pressure of 4.572 km/s. 24 profiles were measured. Measurements were carried out both with the probe and with a hammer. Both measurements gave similar results. The block is composed of three pieces that are 45 cm thick, meaning we are dealing with a composed block. The speed was very low for a limestone, but we cut the block in panels 4 cm thick. The surfaces between smaller blocks were filled with polyester resin. Therefore, the block did not open during multi-blade sawing.



Figure 5: Measurement of the composed block (a, b) and review of the panels after cutting the block (c).



Figure 6: Display of data processing with DataSonic computer programme.

In 2015 we made about 10,100 m^2 of differently thick stone panels with the multi-blade saw, which amounts to 68 blocks. By using ultrasonic measurement of blocks, there has been no breakage of the block on the table so far. Despite some very risky blocks, we have successfully cut and classified them. With the use of measurements certain blocks were also cleaned and we came to the conclusion, that the blocks can also be glued together to fill-up the cutting table. By using ultrasound, we examined whether the surfaces were well lubricated with resin.

In Table 2 the data from previous examinations using ultrasound on different types of natural stone are collected. The natural stone »Lipica rožasti« is characterized by an average passing speed of ultrasonic waves of 5.60 km/s, and the maximum measured speed reached 6.44 km/s. In the »Lipica enotni« we measured an average speed of 5.90 km/s and a maximum speed of 6.45 km/s. For »Repen« an average speed of 6.11 km/s and a maximum speed of 6.60 km/s were measured. All types of stone held up while on the saw and did not open. So far we have made more than 120 measurements of natural stone blocks and thus obtained a large amount of data for making a classifications of natural stone blocks. The aim of the present study was achieved with a good estimate of the blocks and the completion of a technological process, as since we have been using the measurements not one block has opened during the cutting. Table 3 shows the proposal for categorization of natural stone blocks on the basis of preliminary measurements of average velocity of transition of ultrasonic waves. The categorization was made on the basis of the performed measurements and the review of panels after processing the blocks.

For inspection of natural stone blocks we spent 12–15 min on average. The process includes visual and ultrasonic inspection and also gives a more accurate assessment of the quality of the block and reduces the risk of errors.

		Block dimension			Mesured profile			Max. Velocity
Block	Type of material	Length	Width	Height	Velocity by the length	Velocity by the width	Average velocity	
		(cm)	(cm)	(cm)	(km/s)	(km/s)	(km/s)	(km/s)
1	rožasti	285	141	103	2.61	3.50	3.08	-
8	rožasti	300	114	100	6.25	5.90	6.07	-
9	rožasti	259	175	160	5.89	6.28	6.09	-
16	rožasti	260	112	152	6,21	4.55	5.38	6.37
17	rožasti	262	139	158	5.92	4.33	5.12	6.17
18	rožasti	277	122	107	6.25	5.23	5.74	6.40
11	rožasti	303	157	112	6.13	6.05	6.09	6.22
3	enotni	236	98	144	6.11	6.05	5.42	6.12
4	enotni	122	150	90	6.18	5.94	6.06	6.20
10	enotni	142	138	100	6.14	6.20	6.17	6.17
19	enotni	262	118	107	5.7	6.22	5.96	6.45
12	repen	172	173	129	5.99	5.95	5.97	6.08
5	repen	308/240	141	100	6.11	5.16	5.63	6.60
7	repen	175	110	111	7.31	6.22	6.76	7.50
6	repen	315	128	79	6.05	6.08	6.06	6.06
13	repen	200	148	87	6.14	6.16	6.15	6.22

Table 2: The results of previous research on the blocks of natural stone

Table 3: An example of categorization of the natural stone blocks

Category	Velocity (km/s)	Explanation of quality
I.	≥ 6.00	High-quality natural stone block suitable for any thickness, without reinforcement
II.	5.00 ÷ 5.99	Natural stone block, which contains a small veins and changes in the structure, suitable for any thickness without reinforcement
III.	4.00 ÷ 4.99	Natural stone block with bigger cracks, holes, veins, suitable for slabs thicknesses greater than 3 cm
IV.	3.00 ÷ 3.99	Poor quality natural stone block, more irregularities in the structure, and contains a lot of cracks, suitable for slabs thicknesses greater than 4 cm
V.	≤ 2.99	Poor quality natural stone block unsuitable for slabs

Conclusions

To date, there have been many research conducted with various geophysical and other methods, implemented on plates and monuments, but an ultrasound examination of blocks of natural stone – limestone in order to determine their quality or qualification is yet to be done in practice. Relying solely on visual inspection for determining the quality of the blocks is not reliable. Due to deadlines for installing and economical processing of materials, it is necessary to wisely choose the quality of the material for processing and using natural stone blocks.

In reviewing the material we found the following. Many of the pieces need to be sawn through, because of the discontinuities, faults or irregular shapes. For this reason we started manufacturing smaller blocks that are 30-60 cm thick. in order to improve the efficiency of material and improve the material processing prices. For such blocks to be able to supplement the space on a multileaf saw, they were glued together with polyester resin and then cut into panels. Ultrasound examination also gives us an overview of the glued block, as it enables an assessment of whether the contacts between surfaces of the blocks are well filled with resin. The differences in measured speeds are mainly due to defects in materials and different structures of materials, as well as possible errors in performing measurements. The categorization needs to be supplemented with intermediate categories in the future, as in determining the quality of natural stone blocks the shape also plays an important role.

In the future it will also be necessary to add a tomography of blocks, on the basis of measurements, and thus get a picture of where in the materials hazardous areas that need special attention lie.

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Filtration process of industrial gases from dust using basaltic filter

Filtracija prahu iz industrijskih plinov z uporabo bazaltnega filtra

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Abstract

This article presents the results of research and analysis of the use of basalt fibers as a filter material for improving the filtration by modern gas purifying facilities of metallurgical plant foundries of emitted gases from the dust. It is found that the basalt fiber has good porosity due to crystal structure of the fiber and lack of viscosity, as well as high heat resistance due to the high content of SiO, in the Uzbekistan basalts (within 42.7 % and 59.9 %) and TiO₂ (in the range 0.5–2.8 %). The given basalt fiber features allow them form in a simple process of rock processing, in which they take the form of basalt fibers. In the article as one of the conditions of using basalt fibers as a filter material, the possibility of their resistance to high and thermal air flow is indicated. This factor is presented as main technological parameter ensuring the normal operation of the basalt filter material. As a result, it presents data demonstrating the possibility of using basalt filter materials by modern gas purifying facilities of metallurgical plant foundries of emitted into the atmosphere gases from the dust.

Key words: filter, basalt rock, research, gas flow, gas purifying facilities, process variable, filter material

Izvleček

V prispevku so prikazani rezultati raziskave uporabnosti bazaltnih vlaken kot filtrske snovi v sodobnih čistilnih napravah za boljše ločevanje prahu iz plinov, ki izhajajo iz livarn. Ugotovili so, da imajo bazaltna vlakna primerno poroznost spričo njihove kristalne zgradbe ter ustrezno viskoznost in visoko toplotno odpornost zaradi znatne vsebnosti SiO, (v razponu od 42,7 % do 59,9 %) in TiO, (od 0,5 % do 2,8 %) v uzbekistanskih bazaltih. Navedene lastnosti vlaken omogočajo njihovo pridobivanje v enostavnem procesu iz bazalta. V članku poudarjajo kot eno izmed prednosti uporabe bazaltnih vlaken za filtrsko snov njihovo odpornost proti visokotemperaturnemu zračnemu toku. Ta dejavnik predstavljajo kot poglavitni tehnološki parameter, ki zagotavlja normalno delovanje bazaltne filtrske snovi. Prikazani podatki potrjujejo uporabnost bazaltne filtrske snovi v sodobnih čistilnih napravah metalurških livarskih obratov za odstranjevanje prahu iz plinov, ki izhajajo v ozračje.

Ključne besede: filter, bazaltna kamnina, raziskava, plinski tok, čištilne naprave, procesna spremenljivka, filtrska snov

Introduction

Basalt materials have good porosity and lack of viscosity due to the crystal structure of basalt fibers. The crystal structure of basalts is formed during the one-stage processing of rocks in which it takes the fiber form ^[1-4]. This virtually eliminates the possibility of fibers sticking together. The random occurrence of crystal fibers on each other creates favorable conditions for the formation of artificial lattice. The space formed between the fibers while occurrence creates a gap for the free passage of gases through the filter material-walling. The last statement can be grounded by the presence in the filter material of through pores capable of freely let gas pass and thus capture the gas phase dusts.

Experimentally determined that another feature of basalt filter material is that it substantially lacks hygroscopicity and swelling ability. This phenomenon shows that basalt fibers do not absorb moisture and retain their original geometric parameters at any wet environment. Specificity of basalt-fibrous filter material in this case is as follows ^[5]:

- heat-resistance, the value used to determine the coefficient of organic dust capture from harmful gases emission sources of metallurgical plant foundries into the atmosphere;
- relatively high bending stiffness of basalt fibers compared with other mineral fibers, their crystal structure that promote the creation of mechanical strength, high resistance to air flow rate, the lack of stretch factor favoring the formation of an artificial lattice like light mesh that promotes good filtration speed of gases;
- inordinate occurrence of fibers on each other er resulting in the formation of a space between them for the gas flow;
- lack of hygroscopicity and swelling ability, as well as maintaining a constant porosity

of basalt fibers counteract the formation of deposits on the wet gas flow path through the filter at any filtration speed, and provide high filtering efficiency;

 deposits remaining on the filter surface – aerosols can be easily removed from the surface of the basalt-fibrous filter material, blowing them out by compressor air that creates the conditions for its repeated use in the filtering process.

These positive characteristics of basalt-fibrous filter material allow the use of this filter to determine the wash-out rate of harmful organic impurities from the sources of metallurgical plant foundries into the atmosphere. ^[3-4]

Materials and methods

Determination of the mass concentration of dust in the air ^[5]. The technique provides the measuring at the value of the random component of relative error ($\sigma(\Delta^{\circ})$), relative Residual error component (Δc), and total relative error (Δ); in case of the number of parallel observations n = 2 and confidential probability P = 0.95, depending on the range of values of the mass concentration of organic dusts listed in Table 1.

One of the most important moments of basalt-fibrous filter manufacturing is its pressing-in. In the process of pressing-ing and manufacturing basalt-fibrous filter material various minimum pressing force of the packing may be used. They vary depending on the specific and technical conditions, needs, reinforcement, stabilization, etc.

Good chemical resistance of basalt-fibrous filter material extends the scope of application of this material in the presence of high thermal stability.

Basalt filter use happens as follows:

 Basalt filter material together with the protection rings is removed from the plastic bag,

Table 1: Indicators of measurem	ent results' error
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The measurement range of dust mass concentration, mg/m ³	$\sigma_{_{\!arDella}}$	Δc	Δ
0.4-25.0	12.7	2.95	25.4
25.0-50.0	9.0	2.93	18.0

for one hour kept in a laboratory (weighing room) so that it took a room temperature and establishment of balance of air moisture;

- half of the protective rings is opened, the filter element is removed and is piled up using tweezers in four parts;
- The mass of the filter element is weighed. Weighed filter elements using tweezers carefully straightened, put in protection rings and placed in a plastic bag;
- Number of each filter element is recorded on the projecting part of the protective rings, and the resulting mass is accurately recorded in the workbook up to the fourth digit ^[5].
 Filters are delivered to the place of collection in plastic bags.

Determination of the dust concentration in the air is happens follows: an aspirator is switched on and a sample is taken at the breathing zone at a rate 20 dm³/min while controlling the speed rate at all times during the selection. The duration of sampling depends on the degree of dust in the air. Aspirator is switched off after selection and filter is removed from the protection rings on the body; in order to store the collected dust allonge is rotated into a vertical position filter up.

Protection rings are opened, and the filter element is folded in half dusty side inside, and it is clamped in between the protection rings flanges and put in a plastic bag. The air temperature and pressure are noted, sampling time fixed. All the work is performed in accordance with the procedure.

Processing the measurement results was to record the filtration time by stopwatch and comparing with the results of filtering time through a paper filter. To estimate the uncertainty of measurement, we were guided by the following »regulatory documents« ^[3].

In this experimental study, determination of the dust entrainment coefficient at the time of its emission and release into the atmosphere is of practical interest which depends on: the thermal resistance of walls and their stiffness, resistance coefficient, mechanical strength, lack of hygroscopicity and swelling ability, as well as cleanability from impurities for repeated use of the filter materials.

There are a large number of non-woven materials that are used in the gas purifying facilities of pyrometallurgical production, and everywhere they perform important functions such as separation, protection, filtration and drainage. They are not subject decay, impact of mold and mildew, rodents and insects.

Compliance with the above parameters is the basis for the development of new filter objects in the future applicable in gas purification plants foundries of metallurgical enterprises - pyrometallurgical production, which is constantly in need of air filtration materials, since an increase in the production scale of enterprises means and increase of the need for advanced gas purification facilities. Therefore, it is of practical interest to study the work of gas purifying facilities of enterprises, where gas emission and release of harmful contaminants more than permissible are expected.

Application of basalt fibers with high heat resistance is the most appropriate for manufacturing filters for dust entrainment from the exhaust gases of pyrometallurgical production. Table 2 presents the comparative characteristics of the thermal resistance of the proposed basalt-fibrous filter and the current gas purifying facility filter materials ^[2, 4–5].

No	Index of unit strength,		Index of unitThermal stability indexstrength,of current filter, °C			Thermal stability index of basalt filter, °C						
N≌	$N^{\underline{o}}$ kg/mm ²			At a t	At a temperature °C			At a temperature °C				
	Existing	Basaltic	300	400	500	600	700	300	400	500	600	700
Ι	234	242	98.7	88.7	58.9	38.4	25.0	99.7	90.4	63.4	57.8	34.7
II	240	253	99.0	89.0	61.0	39.0	27.0	100	89.3	64.8	44.7	34.1
III	254	259	100	90.0	65.0	38.8	28.6	100	90.0	67.4	43.1	35.8

Table 2: Comparative thermal indices of basalt fibers

From the analysis it is clear that the thermal stability of the basalt filter is not inferior to current filter materials. It can be seen that in both cases, especially Uzbekistan basalt fibers' resistance to heat treatment could reach temperatures above 700 °C.

Technical characteristics of purifying facilities for dust entrainment from chemical harmful gases are shown in Table 3.

The study was conducted according to the procedures and carried out in accordance with the instructions for the technical operation of the filtration materials and under normal climatic conditions (State Standards 15150-69) – offgas temperature from 25 °C to 250 °C, relative humidity (35–90 %) and atmospheric pressure 838–986 mbar (630–740) mm Hg. The results are shown in Table 4.

The presence of through pores in the filter element allows the free passage to air flow yet retaining at the same time the solid particles of the gas phase. It is experimentally found that the filter material of basalt fibers substantially absorbs moisture due to capillarity and has no swelling ability, thus retains its initial geometrical parameters. Compliance with the above mentioned factors facilitates the development of new filtering objects in the future, applicable in gas purification plants of pyrometallurgical production, chemical and cement plants, which constantly are in need of air filter materials.

To investigate the suitability of basalt-fibrous gas purifying filter materials in gas purification plants, three sample filter with different geometrical parameters were prepared.

Three tapes were also prepared, the outer diameter of which corresponds to the inner diameter of the tower, that is, 0.45 m. Then, from the coiled material three samples of basalt fibers were cut.

As a raw material for the production of basalt-fibrous filters, Uzbekistan basalt was used with the following chemical composition, which were investigated in the central research laboratory of the Navoi Mining and Metallurgical Combinat (NMMC) in the range (in %): SiO₂ 42.7–47.3; TiO₂ 0.5–1.51; A1₂O₃ 14.2–20.2; CaO 7.2–8.4; MgO 2.5–3.7; FeO 7.0–8.9; Fe₂O₃ 8.1–9.37; K₂O 0.2–0.5; Na₂O 1.1–2.0 and others that do not affect the quality of the final product.

Considering the fact that during the filtration of liquid mass, the latter is pressed against the filter strongly than the flow of the gaseous

#	Name of index	Unit of measurement	Parameter values
1	The tower diameter for harmful substances emission	m	0.45
2	The tower height for harmful substances emission	m	22
3	The rate of air flow inside the tower	m/s	8.44
4	Exhaust gas temperature	°C	50
5	Diameter basalt filter material – »Stone wool«	m	0.45
6	Thickness of basalt filter material – »Stone wool«	m	0.05

Table 3: Technical characteristics of purifying facilities for dust entrainment from chemical harmful gases

Table 4: Results of a pilot study

N⁰	Selected ingredient	Selection point	Gas temperature, °C	Gas velocity, m/s	Dust concentration, mg/m ³	Amount of gas mixture, m ³ /s	Emission power, mg/s	Gas purification efficiency, %
1	Organic	Inlet	50	8.44	24	1.34	32.21	- FO 1
	dust	Outlet	48	7.24	11.5	1.15	13.24	- 52.1

medium, the compression of basalt fibers was accomplished with a minimum pressure. This is because the filter material can yield positive performance in the event that basalt wool was pressed and dense partition was formed. Samples of compaction effort were selected randomly: in the first sample with a force of 0.5 kg, the second – 2.05 kg and in the third – 3.0 of 5 kg. Then the thickness of molded samples was measured which were equal in m: 0.05, 0.35 and 0.18. Further, in accordance with the existing procedure, measurements were made to detain dust from the gases emitted into the atmosphere through the purifying facilities of pyrometallurgical production foundry. In the first case, the dust emission was found within 50.7–51.8 %. In the second case, the figure was 46.9 % and 44.3 %. In the second and especially in the third case there was a noticeable haze inside the foundry.

Choice of three samples can be argued that the basalt-fibrous filter material was used for the first time and technical parameters of the facility are taken into account. Particular attention was paid to the air flow rate released into the atmosphere, the pressure of the gas medium inside the tower, the geometric characteristics of the tape and filters, pressure + temperature + foundry humidity.

As a result of experimental studies, the acceptability of the use of basalt fibers to meet the challenges of modern gas purifying facilities was established. In practice, it is proved that the accumulation of the particles on a filter, the permeability of the filter material is reduced, so periodically it requires regeneration of filtering object or its replacement.

Research has shown that because of high concentration of dust in the exhaust gases, the low degree of dust entrainment in basalt-fibrous

#	Process name	UOM	Gas purification			
		0011	#1	# 2	# 3	
1.	Filter area	m ²	0.58	0.58	0,58	
2.	Filter thickness	m	0.38	0.28	0.12	
3.	Filter mass	kg	1.60	1.60	1.60	
4.	Filter density	kg/m ³	12	18	22	
5.	Pressing strength	$(kg N)/m^2$	50	205	305	
6.	Entrainment time	min	1.5	1	0.45	
7.	Concentration of hard particles in the air after scrubbing (till purifying using offered method)	g/m ³	18.0	18.0	18.0	
8.	Concentration of hard particles in the air after purification	g/m ³	9.9	8.1	5.4	
9.	Degree of dust entrainment	%	45.0	55.0	70.0	
10.	Specific value of entrainment	g/m ³	0.078	0.095	0.119	
11.	Specific mass capacity of a filter on dust	g/m ³	4.50	3.42	2.17	
12.	Specific volume of the air flow in the pipe	m ³	500	500	500	
13.	Continuous operation of filters with a mass of 1.6 kg at a flow rate of 500 m³/h	d	1.5	2.25	3.0	
13.1	Continuous operation of filters with a mass of 70 kg at a flow rate of 12 points, month	d	3.0	4.5	6.0	
14.	Fraction of solid phase, incl. mm	%	100	100	100	
14.1.	+0.1		58	53	47	
14.2.	-0.1 + 0.74		37	35	28	
14.3.	-0.74 + 0.50		5	11	16	

Table 5: Technical and analytical indicators of experimental filters based on basalt fibers

filters and high resistance of exhaust gases, it is impossible to use offered filters as replacement for the scrubbing system. Therefore it is recommended to use combination filters of different density (number series 1, 2, 3), which allows to extend the use of filters and the degree of tail gas cleanup from dust.

The Table 5 includes technical and analytical indicators of experimental filters on the basis of basalt fibers.

Concentration of hard particles in the flue gas were noticed after their purification by basalt-fibrous filters 1, 2 and 3, which were as follows: (9.9; 8.1 and 5.4) mg/m³, respectively, at an initial concentration of 18.0 mg/m³. Degree of dust entrainment by filters number 1, 2 and 3 were as follows: (45.0; 55.0; 70.0) % respectively. It was also revealed that as the particles accumulated in the filter, the gas permeability of the filtering material is reduced and thus periodically it is necessary to regenerate the filtering object or replace it, which is not that effective.

It is found that continuous work time of filters 1, 2 and 3 with a mass 1.6 kg at a flow rate of the exhaust gas 500 m³/h was (1.5; 2.25 and 3.0) d. In turn, continuous work time of filters 1, 2, 3, with a mass 70.0 kg, at a flow rate of the exhaust gas 500 m³/h is (3.0; 4.5; 6.0) months. It is noted that the method of purification of waste gases from the dust using basalt-fibrous filters after existing wet dust entrainment can increase the degree of purification of flue gases from the dust up to 95-97 % (additional 5-6%), and hence reduce dust emission into the atmosphere in 2.0-3 5 times; it is recommended for pilot testing in experimental and industrial test in Navoi Mining and Metallurgical Combinat (NMMC).

Conclusion

Thus we have proved the suitability of basalt fibers for the manufacture of filter materials for dust removal from flue gases of pyrometallurgical production. It is recommended to use available method of preparing from basalt fibers basalt-fibrous filtering materials that will successfully be applied in the technological processes of mining and metallurgical enterprises.

It was revealed that the quality of producing filter materials can be affected by compression force and for manufacturing filters from basalt-fibrous materials, pressure force up to 0.5 kg is sufficient.

It was found that the crystal structure of the investigated fibers contributed to the formation of sediment layer consisting of solid particles on the filter surface. It is experimentally proved that with increasing speed of the filter process, the amount of dust emitted is increased to a certain point, and then the decrease of the emission is observed. The increase of the emission index and its continuation is the result of the dry sediments influence that created an artificial barrier, at some point began to help the filtration process. Concluding, at the beginning the gas flows through artificially created a layer of sediment, and then through the filtering basalt-fibrous material. In general, it can be considered appropriate manufacturing filtering basalt-fibrous materials that can successfully be used for the emitted industrial gases purification from dust.

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Review paper

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Possibilities of recycling of metallurgical slags and coal mining wastes and reclamation of dumping grounds in Upper Silesian Coal Basin (southern Poland)

Možnost recikliranja metalurške žlindre in premogovniške jalovine ter rekultivacije odvalov v Zgornješlezijski premogovni kadunji (južna Poljska)

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Abstract

The problem of disposing of post metallurgic and coal mining wastes in Upper Silesian Coal Basin (USCB) is discussed. Characteristics of petrographic and mineralogical composition of wastes as well as description of geochemical processes occurring in the waste material are presented. Environmental impacts of waste dumps and threats for the inhabitants living in the neighbourhood of these objects are shown. The possibilities of the secondary use of material collected on the dumps and further reclamation of described areas are indicated.

Key words: post metallurgic wastes, coal mining wastes, dumps

Izvleček

V članku obravnavajo probleme odstranjevanja metalurških in premogovniških odpadkov v Zgornješlezijski premogovni kadunji (ZŠPK). Prikazane so značilnosti mineraloške in petrografske sestave odpadnih snovi in opisani geokemični procesi, ki v njih potekajo, in tudi okoljski učinki teh odvalov in ogroženost prebivalstva, živečega v okolici. Opisane so možnosti sekundarne uporabe materiala z odvalov in rekultivacije prizadetih območij.

Ključne besede: metalurški odpadki, premogovniški odpadki, odvali

Introduction

Field works

Waste dumps resulting from coal mining, steel production and ore exploitation constitute a significant problem for the environmental protection in the Upper Silesia region, which is one of the most industrialized regions of Poland (Figure 1).

The waste dumps, both post-metallurgic and coal mining wastes, are a proof of the mining and processing of hard coal, bog iron ores, zinc and lead ores and accompanying silver ores, conducted since the early middle-ages. It is extremely unsettling that in many Silesian cities dumps as old as 100 years are still present ^[2].

The waste material accumulated for years is made up of a mixture of mining and smelting wastes, disposed in a non-selective manner without any protection of the subsoil. It often happens that at a single dump, wastes resulting from the processing of various ores are present. This is related to the conversions of the former smelters depending on ore availability. Documents have been preserved which provide evidence on the conversion of smelters to enable the processing of ores that were available at the time.

Examined objects considering significant amount of metals or coal in wastes may comprise perspective anthropogenic secondary resources. That is why the question of recovery of secondary materials from dumps with regard to technological possibilities and economical profitability is very important.



Figure 1: Sketch of Upper Silesian Coal Basin (Probierz, Borówka, 2009, modified)^[1].

The record of the old dumps constitutes a significant problem. Current contours of many of the dumps are blurred and it is not possible to determine their precise boundaries (Figure 2). Some of the dumps have suffered denudation due to weathering processes occurring throughout the years. It should, however, be noted that smelting wastes may still be present in the subsoil.

In the past, when the ore deposit was depleted and no new accumulations have been found nearby, it was more profitable to move the entire industrial infrastructure into another place, which – among other things – was caused by the lack of transport routes. Processing of ores was also directly connected to the mining of hard coal, which was used as a furnace fuel – this is why the smelting and mining dumps are often located in close vicinity.

For the needs of inventarization of post-mining and post-metallurgic dumping grounds it was done a literature study, the information was also obtained from administrative units and companies which are the owners of dumps (e.g. coal companies, companies of restructurization of the mines); these data have been verified during field investigations.

According to self study and literature data in the area of Upper Silesia there were recorded:

- 38 waste dumps after metallurgy of Zn-Pb ores as well as steel and iron (Figure 2),
- 41 waste dumps after mining and preparation of Fe ores (Figure 3),

— 231 coal mining waste dumps (Figure 4).
 Altogether in the area of Upper Silesia occur though over 300 waste dumps of different genesis and various composition of wastes.

Non-developed dumps are usually uncovered and their slopes are not protected against crumbling of the accumulated material (Figure 2). In certain locations which are especially prone to weathering, silty forms occur, which are easily blown out and carried by wind. This fosters the distribution of pollution to further areas.

On the surface of dumps' slopes there were observed phenomena similar to gravitational mass movements (landslides). The erosion processes on the slopes were additionally



Figure 2: Zn-Pb wastes on the dump in Ruda Śląska.



Figure 3: Wastes after iron and steel production on the dump in Chorzów.



Figure 4: Burned waste material on coal mining waste dump in Mysłowice.



Figure 5: Coal mining wastes and their contact with surface water. Waste dump in Kaniów.

strengthened by anthropopression (e.g. illegal using of waste dumps for cycling). The erosion troughs situated on one of the dumps had a depth of more than 40 cm.

The water flowing on and infiltrating the wastes causes the washing out of the elements and their migration - especially to the soil environment.

One of the most dangerous environmental impacts of mining wastes is surface water and groundwater pollution (Figure 5). There is a well-known problem of AMD processes (acid mine drainage).

The effect of AMD processes is a contact of sulphur compound, particularly pyrite FeS, with water. Major chemical effects are pH reduction (connected with increased acidity), increase of sulphate, iron, manganese and aluminium contents, oxygen reduction and destruction of the bicarbonate buffering system^[3-6].

The problem of the dumps in the Upper Silesian Coal Basin is a lack of systematic groundwater monitoring on and around the waste dumps as well as legal regulations, concerning particular requirements according to the mentioned above monitoring systems [7].

Recovery of coal may result in changes to the hydrogeochemical profile of the anthropogenic vadose zone, arising from the re-mining and re-disposal of coal extractive waste [4].

Laboratory tests

Despite the passing of years, smelter slag still contains certain amounts of metals ^[8, 9]. Table 1 presents examples of analyses of the chemical composition of Zn-Pb slag (Figure 2) and iron slag (Figure 3).

A significant amount of heavy metals also draws attention. These include Zn, Pb and Cd - especially in the Zn-Pb slag. As a result of the weathering processes, these metals are released from slag components and are carried to the environment along with the solutions. This process is intensified by the presence of sulphur compounds in Zn-Pb slag, the oxidation of which leads to the formation of easily washedout sulphates (Figure 6).

Oxide [mass fractions,%]	Slag after Zn-Pb production (Figure 2)	Slag after steel production (Figure 3)
SiO ₂	19.67	21.75
Al_2O_3	3.58	6.85
Fe ₂ O ₃	23.13	14.28
FeO	6.89	1.51
MnO	0.05	0.90
CaO	5.63	32.14
MgO	5.06	6.76
Na ₂ O	0.85	1.36
K ₂ O	0.16	0.17
SO ₃	10.21	0.58
LOI	22.45	11.70

Table 1: Chemical composition of metallurgical slags – examples of analysis

Element [µg/g]	Slag after Zn-Pb production (Figure 2)	Slag after steel production (Figure 3)
Cd	79.80	3.10
Со	10.00	8.00
Cr	42.00	2 810.00
Cu	71.00	107.00
Ni	80.00	34.00
Pb	7 731.00	1 010.00
Zn	41 500.00	901.00

Self study



Figure 6: Microphotograph of crystals of gypsum in glaze (Zn-Pb slag); transmitted light, magnification 200, one nicol^[2].

In acidic reaction of the environment, the metals are mostly transferred to the soil in the direct vicinity of the dump. The research conducted in this region indicated that the soil around the dumps is characterized by a high level of contamination, especially due to the content of cadmium, which is a particularly toxic element. Iron slag is characterized by a lower concentration of heavy metals such as Cd, Co, Ni, Pb and Zn. However, it shows greater concentration of Cr, which is an element introduced to the furnace charge to improve the properties of the produced steel. It must be noted that iron slag is characterized by a higher value of CaO – 32.14 %, while in the Zn-Pb slag, the CaO content is 5.63 %. The presence of calcium oxide is very favourable, as it has an effect on the preservation of alkaline properties of slag and limits the migration of heavy metals.

Due to the above, it is the iron slag that is considered as a material providing perspectives of application in the production of various kinds of aggregates. Iron slag dumps are thus successively liquidated and the obtained material is used for economic purposes, especially because it is characterized with favourable technical properties. The Zn-Pb dumps still pose a problem and it seems that the most rational solution is the biological restoration of these sites.

Petrographic composition of coal mining wastes

Coal mining wastes represent in majority adjacent rocks, which belong mostly to sedimentary rocks (siltstones, mudstones and sandstones). In the waste material occur also coal shales and significant percentage of coal substance. Detailed values of petrographic composition of coal wastes are presented in the Figure 7.



Explanations: 1 – Siltstones 40–98 % | 2 – Mudstones 2–40 % | 3 – Coal shales 2–25 % | 4 – Sandstones 0–33 %; | 5 – Coal 3–10 %.

Figure 7: Petrographic composition of coal wastes in Upper Silesian Coal Basin.^[10]

Possibilities of the secondary use of material collected on the dumps

There are technical possibilities of recovering of coal from the coal mining waste dumps. The coal recovery reduces also hazards of self-ignition and dump fires. The process of coal recovery is economically justified. From over 230 coal mining dumps in the USCB still remain more than 100 dumps which may be considered as anthropogenic secondary deposits (considering objects which are not thermally active). In the past, there were several examples of successful recovery of coal from the dumps (e.g. Central Mining Waste Dump in Smolnica, waste dumps in Buków – SW of the USCB), some of the dumps are still being exploitated - e.g. a waste dump in Panewniki, a waste dump in Knurów, a waste dump in Czerwionka (a central part of the USCB). The most valuable waste dumps in terms of their recovery are the largest ones. However, it must be taken into consideration other features, e.g. the ownership title, localization, regarding the neighbourhood of protected areas, accessibility and local community interests ^[11]. Due to the fact that the amount of coal in the waste material may be up to 10 % (between 3–10 %, with the assumption that an average amount of coal to be recovered accounts for 5–7 %), it can be estimated that total potential amount of recovered coal from the dumps in the USCB shall account for more than 45 million Mg ^[12].

The dumps of wastes after metallurgy processes represent important potential recovery objects, due to the significant amount of metals (several – dozens percent, regarding mainly lead, zinc as well as other elements, also REE). However, the technology of recovery has not been developed yet. The problem is chemical composition of metals, which are in majority included in the glaze. This problem requires further scientific studies.

Conclusions

In the Upper Silesian Coal Basin, for many years, waste dumps were an integral part of the landscape. But now, due to the environmental activities, the attention has been paid to the environmental hazards, associated with the presence of dumps. These hazards involve mainly water pollution, dust emissions and self-ignition as well as fires of the waste material. On the other hand waste dumps are a potential source of secondary materials which could be use in different sectors of economy. The recovery of coal from wastes disposed on dumping grounds is technically possible and economically justified. The recovery of metals from post-metallurgic dumps has a great potential, but the technology must be developed and requires further studies. It should be remembered that before taking any actions, it is important to know mineralogical and chemical composition of wastes. Basis on such studies, it can be drawn conclusion involving safe utilization of wastes. A very important question is proper reclamation and using of the dumps after successful recovery. These sites may play a new role in the cultural landscape, in a way of creation of new functions – as artistic, cultural, recreation and tourist areas. It should be noted that the most danger for the environment

are old dumps after zinc and lead production. Wastes gathered on them contain a lot of heavy metals, which usually are dispersed in glaze so at present the only rational action to undertake seems to be the creation of a protective layer on the surface of such dumps. The layer should be from soil material of appropriately selected physicochemical parameters, which would ensure favorable conditions for the vegetation of plants. The waste dump should be also isolated by insulation facilities to hinder the migration of the elements to soil.

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Quality of coal and structure of seam 510 (Namurian B) in the Upper Silesian Coal Basin (Poland)

Kakovost premoga in zgradba plasti 510 (namurij B) v Zgornješlezijski premogovni kadunji (Poljska)

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Abstract

Coal seam 510 (Namurian B) is a starting point for limnic sedimentation in the USCB and occupies about 3/4 of USCB's surface, which might reach up to 7 400 km². This coal seam occurs usually among the sandstones of Saddle Beds of the Upper Silesian Sandstone Series and is characterized by considerable thickness, from several meters in the west up to even 24 m in the eastern part of the coal basin. In the east, the coal seam 510 constitutes an equivalent of Saddle Beds (100 % of the thickness of a series is a coal seam) and in the western part, as a result of seam splitting and simultaneous increase of thickness, the coal-bearing capacity decreases to a value of a few percent. In the eastern part of the basin, power coals occur in the coal seam 510, whereas in the west the rank of coals from this seam increases and even coking coals tend to appear.

Key words: Upper Silesian Coal Basin, bituminous coal, coal seam 510, coal quality, quality parameters

Izvleček

Premogova plast 510 (namurij B), s katero se začenja jezerska sedimentacija v Zgornješlezijski premogovni kadunji (ZŠPK), je razširjena na okroglo ³/₄ površine te kadunje, kar ustreza površini blizu 7 400 km². Ta plast je razvita navadno v peščenjakih antiklinalne serije premoških plasti ZŠPK. Zanjo je značilna precejšnja debelina, od nekaj metrov na zahodu do celih 24 m v vzhodnem delu kadunje. Na vzhodu je premogova plast 510 ekvivalent antiklinalnih plasti (100 % debeline serije tvori premogova plast), medtem ko se na zahodu delež premoga zmanjša na vsega nekaj odstotkov zaradi cepitve premogove plasti in hkratnega zvečanja debeline. V vzhodnem delu je surovina v premogovi plasti 510 elektrarniške kakovosti, medtem ko proti zahodu kakovost narašča in doseže celo stopnjo, primerno za koksanje.

Ključne besede: Zgornješlezijska premogovna kadunja, črni premog, premogova plast 510, kakovost, parametri kakovosti

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Introduction

The 510 seam is one of the key seams of the Upper Silesian Coal Basin, which is substantiated both by geological and mining factors. The seam fulfils all conditions of a key seam in a coal-bearing series while maintaining significant (although variable) thickness at a great area of the basin.

From the geological point of view, the 510 seam is a characteristic stratigraphic level constituting a starting point for the sedimentation of limnic deposits formed on the paralic deposits in the USCB. Stratigraphically, the seam represents the saddle beds of the Upper Silesian Sandstone Series of the Namurian B.

The mining factors distinguishing the 510 seam are related to the highest richness in coal (occurring in the seams of the Upper Silesian Sandstone Series, while the coal seams of the Saddle Beds – due to high coal bearing capacity – have constituted one of the most attractive deposit parts from the point of view of mining – although their thickness isn't very high as compared to other seams).

The most disctinctive quality of the 510 seam is its thickness, which reaches up to 24 m in the NE part of the USCB (the Jaworzno region), at a complete reduction of accompanying barren rocks. The 510 seam in this part of the basin thus represents all Saddle Beds (is their equivalent), which – in view of the number of seams and the thickness of barren rock between the seams – fully develops only in the western direction $^{[1,2]}$.

The article presents the occurrence characteristics of the 510 seam within the Polish part of the Upper Silesian Coal Basin.

Geological characteristics of the Upper Silesian Coal Basin

The Upper Silesian Coal Basin (USCB) is one of the most significant Carboniferous basins of Europe. It is located in the area of occurrence of coal-bearing formations of the Carboniferous covering the north-western part of Europe, in the Variscan foredeep. The area of the USCB ranges from 6 100 km² to 7 400 km². This discrepancy results from the difficulty to exactly determine the course of the southern boundary of the basin. The southern boundary of the USCB, which is in the shape of a triangle trough filled with coal bearing upper Carboniferous formations, is conventionally determined by the overthrust line of the Carpathian Mountains.

The USCB represents an orogenic basin type formed in the mountain foredeep of the Silesian and Moravian Variscides area while its sedimentation is characterized by gradual transformation from flysch to molassic coal-bearing formations.

The lithostratigraphic profile (and the geological structure) of the USCB, which has been so far explored by means of > 6 500 boreholes (5 800 in Poland and 700 in the Czech Republic), is comprised of substrata from Precambrian, Cambrian, Devonian, lower Carboniferous and the upper Carboniferous productive series to the overlay seams: Permian, Triassic, Jurassic, Miocene and Quaternary.

The coal-bearing productive formation is comprised of the upper Carboniferous formations indicating significant decrease of thickness in the direction from west to east and a characteristic bipartition in the stratigraphic profile. The lower part of the profile of the coal-bearing formations is characterized by the qualities of the paralic coal-bearing series, while the higher members of the profile include continental limnic deposits. The maximal thickness of the coal-bearing surface reaches up to 8 500 m in the areas of the greatest subsidence (Figure 1). In the coal-bearing formations of the upper Carboniferous (the range of which has been presented in Figure 2), the following lithostratigraphic series may be differentiated (Figure 3): the Paralic Series (Namurian A), the Upper Silesian Sandstone Series (Namurian B and C), the Mudstone Series (Westphalian A and B) and the Cracow Sandstone Series (Westphalian C and D).

The overlay of the productive formation is constituted by the formations of the Permian, Triassic, Jurassic, Tertiary (Miocene) and Quaternary periods ^[2-11].



Figure 1: *Litostratigraphical series of upper and lower Carboniferous periods of the USCB*^[2].



Figure 2: Geological sketch of the USCB^[2].

Location of the 510 seam in the lithostratigrapic profile of the USCB

The formations of the *Upper Silesian Sandstone Series* (Figure 3) are a starting point for the profile of the sediments of the limnic series. In the lower part of the profile, it encompasses Saddle Beds numbered from 510 to 501. These sediments differ from the Paralic Series present lower in the lack of levels with sea fauna and the dominating part of coarse-clastic rocks (conglomerates, sandstones), among which coal seams – usually characterized by high thickness – occur. The seams, as it has it has been mentioned before, are also characterized by high coal bearing capacity. The highest thickness – 1 100 m – is exhibited in the Upper Silesian Sandstone Series in the west part of the basin. Subsequently, the series grows thinner to 480-860 m in the central part and continues to do so in the eastern direction where the seams meet and the series reaches only 300–400 m in thickness (Figure 1). At the NE and E boundary of the USCB, the Upper Silesian Sandstone Series fades and is represented only by the seam 510, 24 m in thickness ^[2].

Saddle Beds are a special case of changes in the thickness of series and splitting of seams in the Upper Silesian Coal Basin (Figure 4). Their maximal thickness reaches 290 m. The key seam of the entire basin – the 510 seam (24 m in thickness) in an equivalent of the entire coal series in the eastern part of the basin (the Jaworzno region, Figure 2). This means that Saddle Beds are represented only by a single seam, while the coal bearing capacity of the Saddle Beds in that region amounts to 100 % ^[1, 2].

In the eastern part of the basin (the Jaworzno region, Figure 2), the Saddle Beds are characterized by variable thickness of series. Their total thickness is from a few meters to 35 m. Their form is a single 510 coal seam, in the roof of which a shoal of clay slate or sandstone is sometimes present. The thickness of the seam is from a few meters to around 24 m.

In the western direction of the basin, the thickness of the Saddle Beds increases and the 510 seam is split.

Initially, in the area of Mysłowice (Figure 2) into two thick 501 and 510 seams with a total thickness of \approx 19.5 m, divided by a small interburden.

In the region of Katowice (Figure 2), the Saddle Beds reach 37–50 m in thickness and incorporate 2 or 3 coal seams characterized by large thickness (501 seams with thicknesses between 3.5 m and 4.0 m and 510 seams with a thickness of 10 m are considered economic).

Two thick seams are also present in the region of Chorzów (Figure 2), with thicknesses of 9.0 m and 2.3 m.

In the region of Zabrze (Figure 2), as many as seven seams have been identified: 501 (thickness of 1.1–1.7 m), 502 (1.2–1.8 m), 503 (1.7–3.2 m), 504 (8.5–12.0 m), 507 (2.6–3.6 m), 509 (3.0–4.6 m) and 510 with a

Figure 3: Stratigraphic division of the Upper Silesian Coal Basin^[2,5,11].

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Another stratigraphic divisions		for Czech part of basin after M. Dopita (1967)								Doubrava Beds	Surcha Upper	Beds Lower	Saddle Beds	Stratigraphic gap	495 Poruba Beds	Jaklovec Beds	Hrusov Beds	095 Petrkovice Beds 005	Kyjovice Beds	Hradec Beds	Moravice Beds	
		for continental sediments after S. Stopa (1957, 1967, 1977)	Stratigraphic gap			Libiąż Beds	n Chełm Beds	20 Łaziska Beds	01 Orzesze Beds	Bebieńsko com 32 Żrzw comitev 337	Swierklany compared 350 Swierklany complex 401 Borynia complex 401	Ruda Beds 40 sensu stricto	Zabrze Beds	for Dąbrowa region*		Grodziec Beds	Flora Beds	Sarnów Beds		Malinowice Beds		
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Figure 4: Schematic drawing of the distribution of saddle beds in the USCB, as provided by different authors [2, 6, 10, 12, 13], simplified and altered.

thickness of 3.8–5.1 m. In total, the Saddle Beds reach up to 32.0 m in thickness. The seams 504 and 510 are assumed to be the key seams characterized by the most stable form.

In the area of Gliwice (Figure 2), the thickness of the Saddle Beds which has formed as a result of the splitting of the 510 seam reaches \approx 220 m and the following groups may be distinguished:

- Szczęsny seams from 501 (with a thickness of \approx 5 m) to 504,
- *Pelagia* with 505–506 seams in the form of lenses,
- *Chrobry,* that is the 507–510 seams.

The total thickness of the seams in these groups reaches 28 m, while the thickness of the 510 seam exceeds 6.3 m.

In the area of Bytom (Figure 2), the thickness of the Saddle Beds (including the 501, 503, 504, 506, 507, 509 and 510 seams) reaches 80–150 m.

In the south-western part of the basin (Jastrzębie region), the thickness of the Saddle Beds reaches 240–290 m^[2].

Coal quality in the 510 seam

The seam encompassing such a great area includes coal characterized by high variability of quality understood as values of quality parameters (Figure 5). The W^a moisture content changes in steps and ranges from 0.7 % to 2.6 % (with one exception of 5.1 %) and by averaging the changes, a weak falling tendency in the southern direction may be noted. This may speak for the occurrence of a weak and slightly irregular Schürmann's rule manifestation – the regular decrease of moisture with the depth of the seam presence.

The A^d ash content in the area of power coals varies in the range between 2.8 % and 7.0 %, exhibiting a mean value of 5.3 %. Significantly higher values, however, have been noted in the area of coking coals.

The V^{daf} volatile matter content is characterized by a regular decrease in the western and southern directions – from 38.7 % to 21.7 %. This may be the evidence of the manifestation of Hilt's law – a regular decrease of V^{daf} along the depth of the seam presence.

The *GCV*^{daf} gross calorific value exhibits a weak growing tendency from 34.8 MJ/kg to 36.6 MJ/kg (departure from this regular tendency is observed only in the regions of Jaworzno and Bytom). The *CV*^{daf} calorific value changes similarly, which is a direct result of the relation between the two parameters (calculation of the values of both these parameters).

Surprisingly, the S_t^{d} total sulphur content also exhibits directionality of changes. A weak growing tendency is observed in the direction from the east to the west and south,




City



E part

aworzno

SW part

Zabrze

Jastrzębie Jastrzębie

40

30

20

0

-10

-20

%-'q





Figure 5: Changes in the quality parameter values of the coal from the 510 seam.

SW part

Zabrze

Bytom

City

City

Katowice

Catowice

(atowice

38

36

34 32

%- ³⁰

26

24

22 20

Jastrzębie Jastrzębie central part

from 0.2 % to 0.5 % (the high value of this parameter in the region of Jaworzno and Katowice constitutes an exception).

Coking indicators, caking capacity in line with the Roga Index and the *FSI* free swelling index exhibit a similar character of changes. The *RI* values initially increase from 29 to 80 and subsequently decrease to 45 and 49. The *FSI* values, however, increase from 1 to 8 $\frac{1}{2}$, and subsequently decrease to 2 and 5.

In case of dilatometric indicators relating to contraction, a growing tendency in the area of power coals from the east to the west may be observed – from 25 % to 36 %. In the area of coking coals, the values of this parameter are lower – in the range of 22-23 %.

The *R* reflectance values in the area of power coals increase from the east towards the west from 0.50 % to 1.04 %.

As mentioned earlier, the thickness of the 510 seam decreases in the western direction. In the region of Jaworzno it is 24 m in thickness, and subsequently the thickness decreases to approximately 10 m and 8 m in the region of Katowice. The minimal thickness – that is 2.8 m – has been found in the region of Bytom. In the southern part of the USCB, in the area of coking coals, the thickness of the seam initially increases to 11 m and subsequently decreases to 6.5 m in the region of Jastrzębie.

Figure 5 schematically presents also the variation in the coal rank. It seems that these changes occur in steps with a growing tendency in the southern direction. In the eastern and central part of the USCB, power coals dominate, while in the SW part coking coals occur.

Conclusions

The 510 seam is one of the key seams of the Upper Silesian Coal Basin from the geological point of view.

Its most characteristic quality is its thickness, which reaches even 24 m in the NE part of the USCB (the Jaworzno region), representing the entire profile of the Saddle Beds, which, in terms of number of seams, develop fully only in the western direction. A weak occurrence of the Schürmann law and a more distinct occurrence of the Hilt's law is observed. The ash content is considerably different in the region of occurrence of power coals (lower values) as compared to the region of coking coal occurrence (higher values). Also a slight yet regular increase of the calorific value, the gross calorific value and the total sulphur content is observed in the direction from the east to the west and south. As far as the coking properties are concerned, lower values are observed in the east and the west, while the highest values are characteristic to the centre of the USCB (the region of Katowice).

The thickness of the 510 seam decreases from 24 m in the east to 3.8 m and 2.8 m in the west and north. In the south, the thickness of the seam reaches the value of 6.5 m and 11.0 m.

A schematic draft of the changes in the coal rank allowed to indicate the fact that the changes occur in steps. In the eastern and central part of the USCB, power coals dominate, while in the SW part coking coals occur.

The article gives consideration only to mean values of the parameters regarding the whole deposit areas (occurring in the regions of particular cities), so that the ranges of the changes and the areas of occurrence of coals (in the view of coalification), are probably broader than presented in the work.

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