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ESTIMATION OF THE CO_2 PROCESS EMISSION IN POLAND GENERATED BY CASTINGS PRODUCTION FROM FERROUS ALLOYS

OSZACOWANIE EMISJI PROCESOWEJ CO_2 Z PRODUKCJI ODLEWÓW ZE STOPÓW ŻELAZA

Data concerning the CO_2 process emission generated by the foundry industry in Poland (processes of steel for castings and cast iron) are presented in the paper. The estimation was performed by means of the method developed by the Authors and based on the balance of elemental carbon in the casting production process. The CO_2 process emission quantity at the casting production from ferrous alloys was 12 518 Mg, in Poland in the year 2006. The process emission factor calculated on this basis was 11.4 kg CO_2/Mg of liquid ferrous alloy. This emission constitutes a negligible fraction – equal only 0.28% of the total Subcategory 2C *Metal Production*. Simultaneously the CO_2 process emission from the decomposition of calcium carbonate ($CaCO_3$) during melting in cupola constitutes only 3% emission from coke combustion in cupola.

Keywords: CO_2 emission, production of castings, greenhouse gases

W artykule zamieszczono dane odnośnie wielkości emisji procesowej CO_2 pochodzącej z przemysłu odlewniczego w Polsce (procesy wytapiania żeliwa i stali na odlewy). Ocena została dokonana przy zastosowaniu metodyki opracowanej przez Autorów, opartej na bilansie węgla pierwiastkowego w procesie produkcji odlewów. W przypadku wytapiania żeliwa uwzględniono emisję CO_2 pochodzącą z rozkładu węglanu wapnia, a dla procesów wytwarzania stali na odlewy emisję pochodzącą z wypalania elektrod węglowych w elektrycznym piecu łukowym oraz emisję pochodzącą z wypalania węgla (operacja świeżenia) ze stali. Wartość emisji procesowej CO_2 z produkcji odlewów ze stopów żelaza w Polsce w roku 2006 wynosiła 12 518 Mg. Obliczony na tej podstawie wskaźnik emisji procesowej wynosi 11,4 kg CO_2/Mg ciekłego stopu żelaza. Emisja ta stanowi znikomy udział wynoszący tylko 0,28% emisji tego gazu z całej podkategorii 2C Produkcja metali. Równocześnie emisja procesowa CO_2 pochodząca z rozkładu $CaCO_3$ w żeliwiaku stanowi tylko 3% emisji CO_2 powstającej podczas spalania koksu w tego typu piecach.

1. Introduction

Development and updating of the estimation methods of the CO_2 emission from foundry processes contributes to the development of the national greenhouse gases (GHG) inventory. The inventory is annually prepared for the national use (among others, for the public statistics) as well as in order to fulfil international obligations of Poland resulting from the ratification of the United Nations Framework Convention on Climate Change (UN FCCC) and the Kyoto Protocol, as well as from the EU Regulation 280/2004/EC concerning the mechanism of greenhouse gases emission monitoring in the European Union and the implementation of the Kyoto Protocol. Estimations of the greenhouse gases emission quantity is being done according to the guidelines of the Intergovernmental Panel on Climate Change (IPCC) approved by the UN FCCC (among others: IPCC 1996 Revised Guidelines, Good Practice Guidance and 2006 IPCC Guidelines for Greenhouse Gas Inventories). According to the binding guidelines [1, 2] the greenhouse gas inventory consists of 6 main IPCC source categories: 1. *Energy* (comprising Fuel Combustion Activities and Fugitive Emission from Fuels), 2. *Industrial Processes* (comprising process emissions), 3. *Solvent and other Products Use*, 4. *Agriculture* (comprising emissions from agricultural activities with the exception of fuel combustion processes), 5. *Land Use, Land Use Change and Forestry* and 6. *Waste* (comprising emissions from waste and sewage management). Main Categories are divided into various Subcategories, where the Subcategory 2.C *Metal Production* comprises, among others, foundry en-

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gineering. Foundry engineering is in Poland an essential branch of metal production, however, in the above mentioned IPCC guidelines there is a lack of specific recommendations concerning the emission estimation methods and emission factors of the greenhouse gases process emission from the casting production. This sector is not considered as the main source of GHG emission and therefore the EU Directive on Emission Trading Scheme does not cover it.

In order to be able to estimate the CO_2 process emission from the foundry industry in Poland and to supplement the inventory in this scope, the authors developed the method based on the elemental carbon balance in the casting production. The method was used for estimating the process emission generated by cast steel and cast iron castings from the entire time period of preparation of inventory reports, it means from the year 1988 to the year 2006.

The greenhouse gases process emission includes only the emission generated by the given technological process excluding emissions from the fuel combustion for purely energy related processes (e.g. coke burning in cupolas), or emissions generated by the power engineering production used for the power supply of melting furnaces. Calculations of the CO_2 emission concern only melting processes of ferrous alloys since they are the main sources of process emissions. The CO_2 emissions occurring at pouring into moulding sands containing organic binding agents or sands with bentonite and coal dusts were not taken into consideration as not being of any significant value.

As the source of the CO_2 process emission from steelmaking processes the following was assumed:

- in the case of cast iron making: emission originated from the decomposition of calcium carbonate ($CaCO_3$) during melting in cupola,
- in the case of steelmaking for castings: emission originated from burning carbon electrodes during a steel heating in an electric arc furnace as well as emission generated by burning out carbon from steel (oxidising process).

2. Casting production from ferrous alloys in Poland

The list of production quantities of castings from ferrous alloys in Poland during the years 1988-2006 is presented in Table 1. On the basis of these data and of the assumed metal yield the amount of liquid metal obtained in individual alloy categories was calculated. The metal yield was defined as follows:

Metal yield = (Mass of sound castings) x 100% : (Mass of melted metal)

As far as the CO_2 emission quantity is concerned the amount of liquid metal made in individual kinds of melting furnaces is significant. Due to the lack of data related to metal yields in the years 1988 - 2002 the average value from the years 2003-2005 was applied. For the year 2006 the yield indices from the year 2005 were used. Under such assumptions the average yield from ferrous alloys was 59.4% in 2005 and 58.9% in 2006.

3. CO_2 process emission from iron castings production

It was assumed, that in the process of cast iron making, the sole source of the CO_2 process emission is the decomposition of calcium carbonate in cupolas. On the basis of the coke consumption in Polish foundry plants and indices of coke and $CaCO_3$ fractions in a charge the consumption of calcium carbonate in each year was calculated. The average coke fraction in a charge was assumed as 15 kg of coke/100 kg metal charge and the $CaCO_3$ fraction was taken as 25 kg $CaCO_3$/100 kg of coke, which means 3.75 kg $CaCO_3$/100 kg of metal charge [3, 4]. The liquid metal yield from the cupola was assumed to be 95%, which corresponds with the melting loss being 5%. In addition, it was assumed that the coke used in cupolas contains 85-90% of C. The CO_2 emission originated from the decomposition of $CaCO_3$ is shown in Table 2. The CO_2 emission in the year 2006 was nearly 5-times smaller than the one in 1988 equalling 6 380 Mg. This is related to a decreasing participation of the casting iron production in cupolas (in 1988 it was approximately 80%, while in 2006 less than 40%) and to the smaller production of cast iron (more than 2-times). A systematic, however rather slow, tendency of decreasing the quantity of cast iron made in cupolas as compared to the total quantity of cast iron can be observed. Induction furnaces are nowadays dominating in this field. Therefore, it might be reasonably to assume that the quantity of CO_2 emitted from cupola processes will be gradually decreasing in the future.

4. CO_2 process emission at steelmaking for castings

It was assumed that – in Poland – 97% of steelmaking for castings is produced in electric arc furnaces, while 3% in induction furnaces. A source of the CO_2 process emission at steelmaking in electric arc furnaces is burning of electrodes and an oxidation process. It was assumed that the average wear of electrodes is 8 kg/Mg of liquid steel (according to the BREF Reference Document [1] the wear equals 3 - 10 kg/Mg of liquid steel, while according to the information collected in national

TABLE 1

Production of ferrous castings in Poland (1988–2007)

Year	Cast iron											Cast steel			Total	
	Gray iron			Ductile iron			Malleable iron			Total					Ferrous casting	
	Castings [Mg]	Yield [%]	Liquid metal [Mg]	Castings [Mg]	Yield [%]	Liquid metal [Mg]	Castings [Mg]	Yield [%]	Liquid metal [Mg]	Castings [Mg]	Liquid metal [Mg]	Castings [Mg]	Yield [%]	Liquid metal [Mg]	Castings [Mg]	Liquid metal [Mg]
19881[1]	1 325 125	69[b]	1 920471	63 032	49.6[b]	127 083	45 842	33.2[b]	138 079	1 434 000	2 185 633	285 000	44.4[b]	641 892	1 719 000	2 827 525
1989[2]	1 125 063		1 630526	53 516		107 897	38 921		117 232	1 217 500	1 855 655	239 000		538 289	1 456 500	2 393 943
1990[3]	925 000		1 340580	44 000		88 710	32 000		96 386	1 001 000	1 525 676	193 000		434 685	1 194 000	1 960 361
1991[4]	608 650		882 101	34 500		69 556	29 000		87 349	672 150	1 039 006	100 330		225 968	772 480	1 264 974
1992[5]	582 640		844 406	37 650		75 907	30 820		92 831	651 110	1 013 144	73 600		165 766	724 710	1 178 910
1993[6]	563 390		816 507	52 040		104 919	28 070		84 548	643 500	1 005 9784	66 810		150 473	710 310	1 156 447
1994[7]	584 000		846 377	59 000		118 952	30 620		92 229	673 620	1 057 558	71 000		159 910	744 620	1 217 468
1995[8]	625 000		905 797	70 000		141 129	30 050		90 512	725 050	1 137 438	78 100		175 901	803 150	1 313 339
1996[9]	554 800		804 058	96 400		194 355	24 900		75 000	676 100	1 073 413	86 100		193 919	762 200	1 267 332
1997[10]	507 000		734 783	120 000		241 935	25 900		78 012	652 900	1 054 730	79 200		178 378	732 100	1 233 108
1998[11]	460 000		666 667	81 000		163 306	24 650		74 247	565 650	904 220	62 200		140 090	627 850	1 044 310
1999[12]	450 000		652 174	86 500		174 395	18 700		56 325	555 200	882 894	55 000		123 874	610 200	1 006 768
2000[13]	510 000		739 130	90 500		182 460	20 300		61 145	620 800	982 735	55 400		124 775	676 200	1 107 510
2001[14]	495 000		717 391	105 200		212 097	18 300		55 120	618 500	984 608	54 500		122 748	673 000	1 107 356
2002[15]	428 000		620 290	105 500		212 702	14 600		43 976	548 100	876 968	48 400		109 009	596 500	985 977
2003[16]	423 000	67	631 343	93 200	50.3	185 288	15 700	32.3	48 607	531 900	865 238	46 500	41.7	111 511	578 400	976 749
2004[17]	445 000	72	618 055	97 500	47.9	203 549	24 930	34.5	72 261	567 430	893 865	54 100	46.1	117 354	621 530	1 011 219
2005[18]	428 000	68.1	628 488	112 000	50.7	220 907	21 500	32.9	65 350	561 500	914 745	60 600	45.5	133 187	622 100	1 047 932
2006[19]	431 000	68.1[a]	632 893	129 400	50.7[a]	255 227	24 400	32.9[a]	74 164	584 800	962 284	60 400	45.5[a]	132 747	645 200	1 095 031
2007[20]	453 000	68.1[a]	665 198	148 600	50.7[a]	293 097	20 000	32.9[a]	60 790	621 600	1 019 085	64 700	45.5[a]	142 198	686 300	1 161 283

Assumptions

a) Assumed yield for 2005.
b) Assumed yield as a average for 2003-2005.
c) Metal yield = (Mass of sound castings) x 100% : (Mass of melted metal)

1) Grey iron, ductile iron, alloy iron and malleable iron. (Modern Casting 12/1989)
2) Approximate data (average from 1988 and 1990)
3) Modern Casting 12/1991
4) Modern Casting 12/1992
5) Modern Casting 12/1993
6) Modern Casting 12/1994
7) Modern Casting 12/1995
8) Modern Casting 12/1996
9) Modern Casting 12/1997
10) Modern Casting 12/1998
11) Modern Casting 12/1999
12) Modern Casting 12/2000
13) Modern Casting 12/2001
14),15),16),17),18) Foundry – Science and Practice (Odlewnictwo – Nauka i Praktyka *in Polish*) 2003, 2004, 2005, 2006, 2007
19) Modern Casting 12/2007
20) Modern Casting 12/2008

casting houses that wear is at the level between 6 and 12 kg/Mg of liquid steel). The level of burning out of carbon from steel (oxidation process) in an electric arc furnace was assumed to be 0.5% (which means 5 kg/Mg

TABLE 2

Consumption of coke and CO_2 – process emission (from $CaCO_3$ decompresition) in cast iron production

Year	Coke consumption, [Mg]	$CaCO_3$ consumption[a)], [Mg]	CO_2 emission from $CaCO_3$ break down, [Mg]	Metal charge into cupola, [Mg]	Amount of liquid cast iron melted in cupola[b)], [Mg]	Total amount of liquid cast iron [Mg]	Part of liquid cast iron melted in cupola[c)], [%]
1988[1]	276 080	69 020	30 369	1 840 533	1 748 506	2 185 633	80
1989[2]	234 399	58 560	25 784	1 562 657	1 484 524	1 855 655	
1990[3]	192 717	48 179	21 199	1 284 780	1 220 541	1 525 676	
1991[4]	131 243	32 811	14 437	874 952	831 205	1 039 006	
1992[5]	127 959	31 990	14 075	653 058	810 405	1 013 144	
1993[6]	127 070	31 768	13 978	847 136	804 779	1 005 974	
1994[7]	133 586	33 397	14 694	890 575	846 046	1 057 558	
1995[8]	143 676	35 919	15 804	957 842	909 950	1 137 438	
1996[9]	135 589	33 897	14 915	903 927	858 730	1 073 413	
1997[10]	133 229	33 307	14 655	888 194	843 784	1 054 730	
1998[11]	114 217	28 554	12 564	761 448	723 376	904 220	
1999[12]	93 000	23 250	10 230	620 000	589 000	882 894	66.7
2000[13]	120 000	30 000	13 200	800 000	760 000	982 735	77.3
2001[14]	82 000	20 500	9 020	546 667	519 334	984 608	52.7
2002[15]	72 000	18 000	7 920	480 000	456 000	876 968	52.0
2003[16]	65 200	16 300	7 172	434 667	412 934	865 238	47.7
2004[17]	62 400	15 600	6 864	416 000	395 200	893 865	44.2
2005[18]	58 400	14 600	6 424	389 300	369 835	914 745	40.4
2006[20]	58 000	14 500	6 380	386 667	367 334	962 163	38.2

Assumptions

a) Part of $CaCO_3$ in charge is 25% of coke addition (3.75% of metal charge).
b) Yield of liquid metal from cupola is 95% (melting loss 5%).
c) For 1988 - 1998 80% fraction of cast iron melted in cupola was assumed 80%.
d) Coke for charge contains 85-90% C.
e) For 1988 - 1998 consumption of coke and CaCO3 was calculated from an average part of cast iron melted in cupola as 80%.
f) For 1999 - 2006 part of cast iron melted in cupola was calculated from the consumption of coke.
Data from Table 1 in the literature.

of liquid steel). At such assumptions – for the amount of steel made in arc furnaces in Poland in the year 2007 being 132 932 Mg – the total CO2 process emission was 6 575 Mg, out of which 4 406 Mg – from the electrode wear and 2 529 Mg – from the oxidation process.

TABLE 3

CO_2 emission from burning out of electrodes and carbon from melting of steel in electric arc furnace (1988 – 2007)

Year	Liquid steel [Mg]	Liquid steel melted in electric arc furnace[a)], [Mg]	Liquid steel melted in induction furnace[a)], [Mg]	Electrode wear[b)], [Mg]	CO_2 emission from burning out of electrodes, [Mg]	Amount of carbon burn out[c)], [Mg]	CO_2 emission from burn out of carbon, [Mg]	Total CO_2 emission from melting of steel, [Mg]
1988[1]	641 892	622 635	19 257	4 981	18 264	3 113	11 415	29 679
1989[2]	538 289	522 140	b.d.	4 177	15 316	2 611	9 573	24 889
1990[3]	434 685	421 644	13 041	3 373	12 368	2 108	7 730	20 098
1991[4]	225 968	219 189	6 779	1 754	6 430	1 096	4 018	10 448
1992[5]	165 766	160 793	4 973	1 286	4 717	804	2 948	7 665
1993[6]	150 473	145 959	4 514	1 168	4 281	730	2 676	6 957
1994[7]	159 910	155 113	4 797	1 241	4 550	776	2 844	7 394
1995[8]	175 901	170 624	5 277	1 365	5 005	853	3 128	8 133
1996[9]	193 919	188 101	5 818	1 505	5 518	941 3	450	8 968
1997[10]	178 378	173 027	5 351	1 384	5 075	865	3 172	8 247
1998[11]	140 090	135 887	4 203	1 087	3 986	679	2 491	6 477
1999[12]	123 874	120 158	3 716	961	3 525	601	2 203	5 728
2000[13]	124 775	121 032	3 743	968	3 550	605	2 218	5 768
2001[14]	122 748	119 066	3 682	953	3 493	595	2 183	5 676
2002[15]	109 009	105 739	3 270	846	3 102	529	1 939	5 041
2003[16]	111 511	108 166	3 345	865	3 173	541	1 983	5 156
2004[17]	117 354	113 833	3 521	911	3 339	569	2 087	5 426
2005[18]	133 187	129 191	3 996	1 034	3 790	646	2 369	6 158
2006[19]	132 747	128 765	3 982	1 030	3 777	644	2 361	6 138
2007[20]	142 198	137 932	4 266	1 103	4 046	690	2 529	6 575

b.d. – brak danych

Assumptions

a) In electric arc furnaces 97% steel for cast steel is melted and in induction furnace only 3%.
b) Average consumption of electrodes in electric arc furnace was assumed as 8 kg/Mg of liquid steel (according to BREF 3 -10 kg/Mg liquid steel and in Polish foundry 6 - 12 kg/Mg liquid steel).
c) During melting of steel in electric arc furnace 0.5% of carbon average (5 kg/Mg liquid steel burns out).

5. Conclusions

The CO_2 process emission generated by casting production from ferrous alloys in Poland in the year 2006 was equal 12 518 Mg (it originated from the process of cast iron making in cupolas and from the steelmaking process in electric arc furnaces whereas the participation of both sources was very similar). The emission factor calculated on this basis is equal to 11.4 kg CO_2/Mg of liquid ferrous alloy. The tendency of a decreasing fraction of cast iron produced in cupolas, as compared to the total steelmaking production, observed in the last couple of years will result in a decrease of the CO_2 emission from this process. The fraction of the CO_2 process emission from the casting production from ferrous alloys is quite small and according to the results of the national inventories of greenhouse gases was bellow in 2006 [5] 0.07% of the CO_2 emission estimated for the Category 2 IPCC *Industrial processes* (emission fractions from steelmaking and cast iron production were alike – approximately 0.03% each) (Fig. 1), while the total CO_2 emission from the whole Category 2 comprises approximately 5.8% of the total national emission of this gas (Fig. 2). The presented in Fig. 2 fractions of the particular main IPCC Categories in the national carbon dioxide emission do not take into consideration the CO_2 emission/absorption from Sector 5 *Land Use, Land Use Change and Forestry*; Sector 4 *Agriculture* was taken into consideration, however the CO_2 emission is not estimated for this Sector, since it is assumed that carbon dioxide emitted during a biomass burning is absorbed by plants in the subsequent vegetation period.

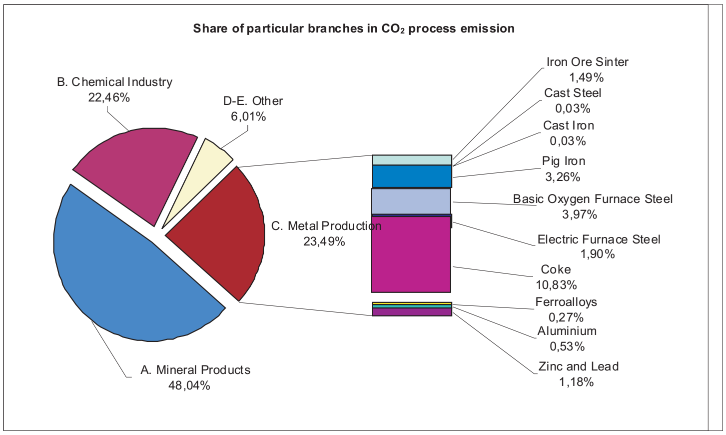

Fig. 1. Fractions of individual sub-sectors of the IPCC Category 2 *Industrial Processes* in the CO_2 emission in 2006 [5]

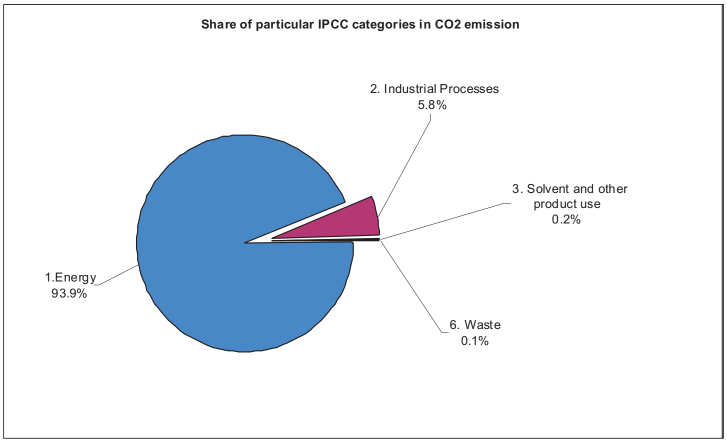

Fig. 2. Fractions of individual IPCC Categories in the CO_2 emission in Poland (with the exception of Category 5. *Land Use, Land Use Change and Forestry*) in 2006 [5]

Even in the Subcategory 2.C *Metal Production* the production of castings from ferrous alloys is not a significant source of the CO_2 emission since it is estimated that the frctions of cast steel and cast iron production are 0.14 % each of the total Subcategory.

Simultaneously, the CO_2 process emission from the decomposition of calcium carbonate ($CaCO_3$) during melting in cupola constitutes only 3% emission from coke combustion in cupola.

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STRUCTURAL EXAMINATION OF THE CROSS-LINKING REACTION MECHANISM OF POLYACRYLATE BINDING AGENTS

BADANIA STRUKTURALNE NAD MECHANIZMEM REAKCJI SIECIOWANIA SPOIW POLIAKRYLANOWYCH

The results of structural investigations (FTIR, Raman, NMR) performed in order to determine mechanisms of cross-linking reactions of samples of polyacrylic binding agents: sodium polyacrylate. Chemical methods ($Ca(OH)_2 + CO_2$) as well as physical ones (microwave and UV radiations) were applied as cross-linking factors.

During the chemical cross-linking reaction of sodium polyacrylate by means of $Ca(OH)_2$ and CO_2 divalent Ca^{2+} cations are built-in into a polymer chain in place of monovalent Na^+ cations. The reaction is ionic and no changes in the position of absorption bands - before and after cross-linking – are seen on the obtained spectra.

The cross-linking reaction of sodium polyackrylate by electromagnetic radiation (microwaves and UV) occurs with a formation of new chemical bonds with a participation of carbonyl groups (ester, anhydride, aldehyde or ketone). Position changes of absorption bands before and after the cross-linking reaction are observed on the obtained spectra.

In cross-linking done by microwaves the active centres on polymer particles are formed. Atomic excitations and the polymer reactivity increase occurs simultaneously and as the result the cross-linking reaction between polymer chains takes place (with a participation of carboxyl or carboxylate groups).

The cross-linking reaction by the UV radiation occurs with the formation of active radicals in polymer particles. Those radicals can further react with each other an in consequence the cross-linked product of a complicated structure is formed.

The performed structural examinations have proved that the kind of the applied cross-linking factor is essential for the reaction mechanism as well as for the final physical and chemical properties of the hardened moulding sands.

Keywords: polyacrylates, cross-linking, microwaves, UV radiation, foundry engineering

W prezentowanym artykule przedstawiono wyniki badań strukturalnych (FTIR, Raman, NMR) wykonanych w celu opracowania mechanizmu reakcji sieciowania próbek spoiwa poliakrylanowego: poli(akrylan sodu) Sokalan CP10, BASF. Jako czynniki sieciujące zastosowano metody chemiczne ($Ca(OH)_2 + CO_2$) oraz fizyczne (promieniowanie mikrofalowe, promieniowanie UV).

W procesie sieciowania chemicznego poli(akrylanu sodu) za pomocą $Ca(OH)_2 + CO_2$ następuje wbudowywanie się w łańcuch polimerowy dwudodatnich kationów Ca^{2+} w miejsce jednododatnich kationów Na^+. Reakcja ma przebieg jonowy i nie obserwuje się zmian w położeniu pasm absorpcyjnych przed i po sieciowaniu na otrzymanych widmach.

Reakcja sieciowania poli(akrylanu sodu) promieniowaniem elektromagnetycznym (mikrofalowym i UV) zachodzi przy utworzeniu nowych wiązań chemicznych z udziałem grupy karbonylowej (grupy estrowe, bezwodnikowe, aldehydowe, ketonowe). Na otrzymanych widmach obserwuje się zmiany w położeniu pasm absorpcyjnych przed i po sieciowaniu związane z przebiegiem reakcji sieciowania.

W procesie sieciowania mikrofalami poli(akrylanu sodu) powstają centra aktywne w cząsteczkach polimeru. Zachodzi jednoczesne wzbudzenie atomów oraz wzrost reaktywności polimeru, a w następstwie reakcja sieciowania między łańcuchami polimerowymi z udziałem grup karboksylowych lub karboksylanowych.

Reakcja sieciowania poli(akrylanu sodu) promieniami UV przebiega z utworzeniem w cząsteczkach polimeru aktywnych rodników, które dalej mogą ze sobą reagować, co w konsekwencji prowadzi do powstania usieciowanego produktu o skomplikowanej strukturze.

Przeprowadzone badania strukturalne dowiodły, że rodzaj zastosowanego czynnika sieciującego ma istotny wpływ na mechanizm reakcji sieciowania polimeru, jak również na późniejsze właściwości fizykochemiczne utwardzonej masy odlewniczej.

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1. Introduction

Reference data [1, 2, 3] indicate that cross-linking of polymer plastics can be done by various ways: in chemical reaction (poly-condensation, copolymerisation), under a temperature or electromagnetic radiation influence. Strong covalent bonds formed in cross-linking reactions have a substantial influence on the final mechanical properties, especially strength, of the polymer. Weaker ionic bonds, especially hydrogen bonds form reversible lattices, which at higher temperatures are melting without decomposition and return into the lattice state after cooling. During cross-linking of macromolecules also weaker secondary chemical bonds such as hydrogen bonds, van der Waals intermolecular forces, or lateral covalent bonds (Fig.1) are formed. Products formed in actual cross-linking processes contain various structures different than the ideal lattice.

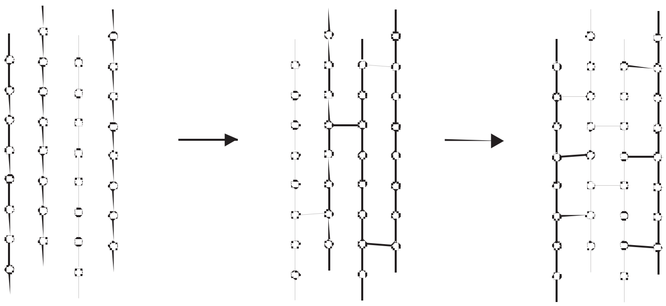
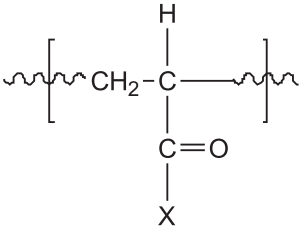


Fig. 1. Cross-linking of long-chain molecules [1]

Acrylic polymers obtained from acrylic acid and its derivatives such as esters, amides or chlorides are characterized by the mer structure presented in Fig. 2 (acrylic series), where X can be: -OH, -OMe, -OR, $-NH_2$ or -Cl [1].



$$\sim\left[\mathrm{CH_2}-\overset{\mathrm{H}}{\underset{\underset{\mathrm{X}}{\mathrm{C{=}O}}}{\mathrm{C}}}-\right]\sim$$

Fig. 2. General formula of an acrylic polymer

Acrylic acid polymers, due to their physical and chemical properties, have found application in several industry branches [5, 6, 7, 8]. Foundry engineering is one of the fields where trials of the technological utilisation of acrylic polymers were undertaken. Those polymers are applied as binding agents in castings (moulding and core sands) [7, 9, 10, 11].

Investigations on applying various cross-linking methods of binding agents from the group of acrylic polymers and attempts of the explanation of their cross-linking mechanisms were undertaken in the paper.

2. Investigation methodology

Materials

The following samples were used in tests:

1. Binding agent: sodium polyacrylate, Sokalan CP10, molar mass 4 000 g/mol, concentration 45 %, pH 8.5, viscosity 500 mPa.s, produced by BASF Company;
2. $Ca(OH)_2$ (analytically pure), Polish Chemical Reagents S.A. Gliwice;
3. CO_2 gas.

Cross-linking of samples

The list of the applied cross-linking methods together with the equipment used and cross-linking conditions is given in Table 1. Structural tests were performed after the cross-linking procedure.

TABLE 1

List of the applied cross-linking methods

Hardening factor	Equipment	Conditions of hardening
CO_2	Run-purging device supplying CO_2	CO_2 run-purging time 60 s
Microwaves	Microwave device RM 2001 Pc of Plazmatronica Company	Microwave power 800 W Time of operation 150 s
UV radiation	Photochemical reactor RAYONET	Wave length 300 nm Time of operation 1h

3. Structural investigations

Spectroscopic tests in **infrared FT-IR** were carried on by means of the spectrometer Digilab Excalibur FTS 3000 Mx with detector DTGS, electrically cooled. This spectrometer is equipped with two attachments: ATR with ZnSe crystal for multiple reflection and the transmission attachment.

Raman spectroscopic measurements were performed by the trinetlike spectrometer of the Yobin Yvon Company, model T64000 and the Fourier spectrometer of the Bio-Rad Company.

13C NMR spectra of the tested polymers were obtained by the Bruker AMX spectrometer 500 MHz. Polymer samples were dissolved in D_2O. All measurements were done at the room temperature.

4. Structure analysis of samples chemically cross-linked – with the participation of calcium cations

FT-IR spectra of sodium polyacrylate before and after cross-linking performed by means of calcium hydroxide and CO_2 in the range of 4000-400 cm^{-1} are presented in Figure 3. A wide band corresponding to stretching vibrations of the hydroxyl group (band of a free OH group [from water] and hydrogen bonds) occurs in the range of wave number 3700-3000 cm^{-1}. Negligible differences in the shape of this band – before and after the cross-linking – are the result of -OH groups participation in hydrogen bonds. Characteristic absorption bands at the wave number 1651 cm^{-1} corresponding to deformation vibrations C-OH and two bands at 1559 cm^{-1} and 1324 cm^{-1} typical for salts of carboxylic acids (symmetrical stretching vibrations of carboxyl anions -COO^{-}) occur on the obtained FT-IR spectra. Small changes in the shape of those bands indicate structural and conformation changes occurring during material hardening and are solely related to building-in of Ca^{2+} cations in place of Na^{+} cations in a polymer chain. The band corresponding to stretching vibrations of C-O bond and deformation vibrations of C-O-H group occurs at the wave number 1246 cm^{-1}. An exchange of ions is accompanied by conformation changes in the polymer structure, what exhibits itself in a general shape of spectra. However, there are no changes in absorption band positions before and after cross-linking.

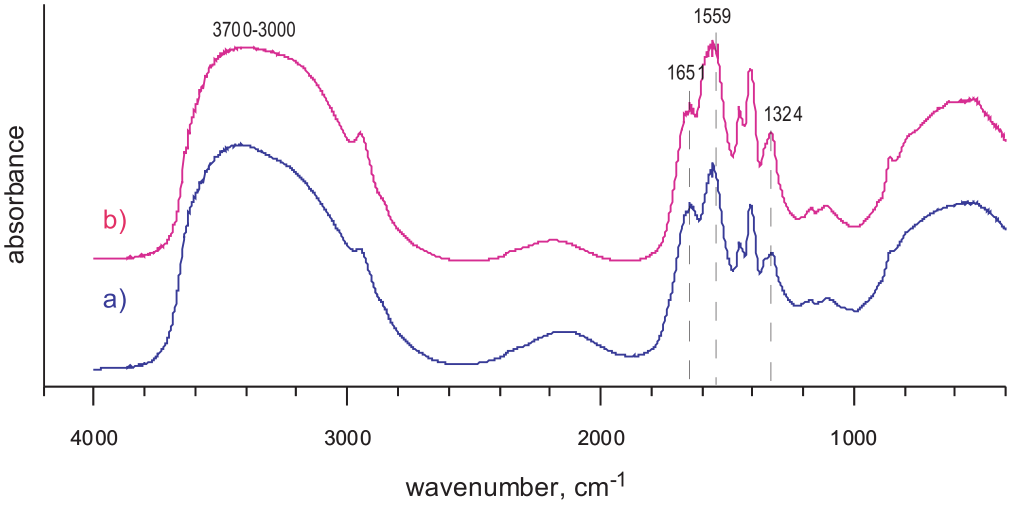


Fig. 3. FT-IR spectra: a) sodium polyacrylate solution, b) sodium polyacrylate solution $+Ca(OH)_2+CO_2$

Polyacrylate structure before and after cross-linking was confirmed on the basis of ^{13}C NMR spectrum. Signals at 184.8 ppm and 183.4 ppm originated from carbon atoms of carbonyl group in carboxylic acids are seen in NMR spectrum presented in Figure 4.

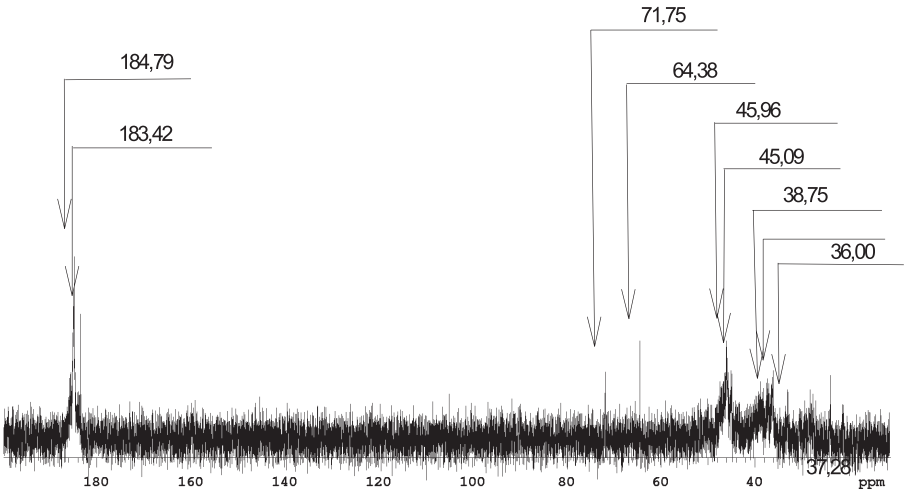


Fig. 4. ^{13}C NMR spectrum of sodium polyacrylate solution in D_2O

Three signals 64.38 ppm, 45.9 ppm and 45.1 ppm can be assigned to C_α carbon atoms while signals 38.7 ppm, 37.3 ppm, 36 ppm belong to C_β carbon atoms (Fig. 5).

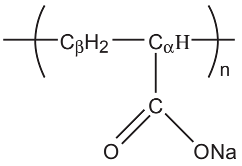


Fig. 5. Sodium polyacrylate structure

After polyacrylate cross-linking by means of $Ca(OH)_2$ with the participation of CO_2 – on the NMR spectrum presented in Figure 6 – a decrease of the signal intensity from -C=O group ($\delta^{1)}$=184.9 ppm, δ=183.4 ppm) can be noticed. Additionally the weak signal appears at 183.9 ppm. This new signal occurring in the NMR spectrum – after hardening – is probably related to calcium atoms building-in into a polymer chain. A weak signal at 45.6 ppm originates from C_α carbon atoms and a signal at 36 ppm from C_β carbon atoms (Fig. 6). A decrease of number and intensity of signals in this spectrum can be explained by more difficult (after hardening) solubility of calcium polyacrylate sample in D_2O.

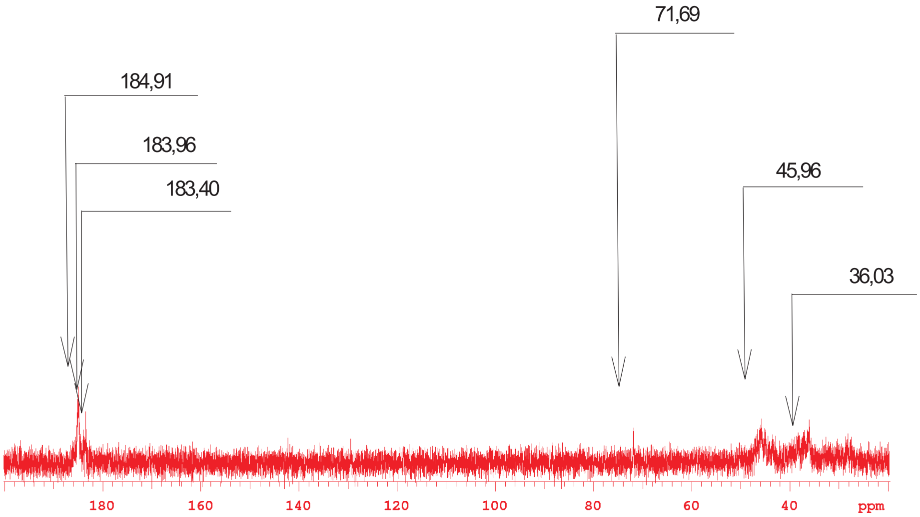


Fig. 6. ^{13}C NMR spectrum of sodium polyacrylate + $Ca(OH)_2$+CO_2 solution in D_2O

[1)] δ – chemical shift – determines the difference in constant screening of the nucleus in a standard and in a sample. δ value is an abstract number of the order 10^{-6}, thus, pseudo-unit "part per million" [ppm].

5. Structure analysis of samples cross-linked by the microwave radiation

Figure 7 presents FT-IR spectra of sodium polyacrylate sample cross-linked by means of microwaves in the range of 4000-400 cm^{-1}. A decrease of the absorption band corresponding to stretching vibrations of -OH groups, caused by water evaporation due to microwaves action, can be seen in the range of wave numbers 3700-2900 cm^{-1}. The absorption band of sodium polyacrylate solution at 1557 cm^{-1} (spectrum a) corresponding to asymmetric vibrations of COO^{-} during cross-linking by microwaves shifts in the direction of a higher wave number 1567 cm^{-1} (spectrum b), while the band at 1651 cm^{-1} (deformation vibrations of C-OH) smears and shifts with an additional appearance of a broad band at 1750 cm^{-1} (spectrum b). The formed smeared band has no distinct maximum. Those changes can be the result of overlapping of vibrations related to the formation of new bonds with the participation of carbonyl group (of ester or anhydride type).

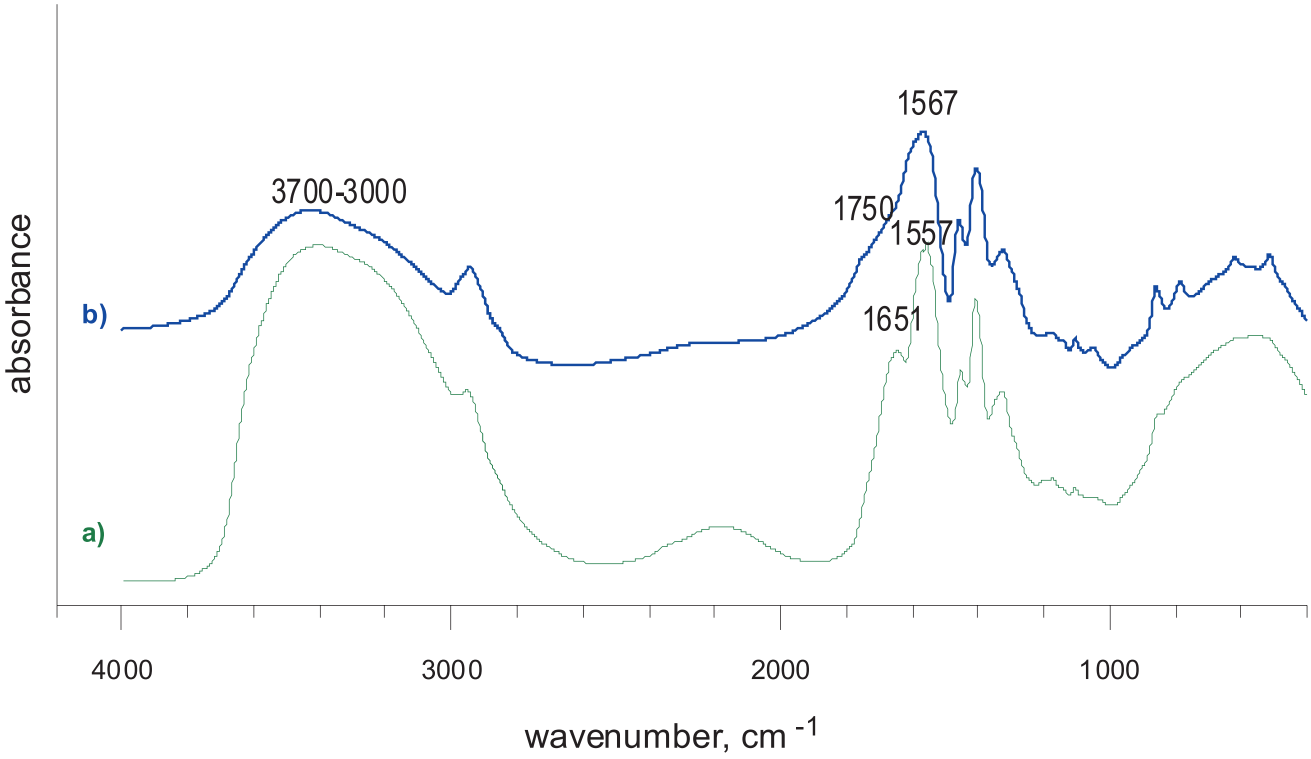


Fig. 7. FT-IR spectra: a) sodium polyacrylate solution), b) sodium polyacrylate solution + microwaves

On the Raman spectra (Fig. 8) within wave numbers 3700-2900 cm^{-1} a decay of an absorption band corresponding to stretching vibrations of -OH groups (3420 cm^{-1}) – in the case of cross-linking done by microwaves – can be seen (spectrum b). The absorption band at 1583 cm^{-1} shifts in the direction of higher wave numbers (spectrum b: 1613 cm$^{-1)}$, while the band within wave numbers 1358-1320 cm^{-1} (spectrum a) is shifted towards lower wave numbers (spectrum b: 1337 cm$^{-1)}$. It can be assumed that band shifts are the result of overlapping of vibrations related to the new ester bonds formation during the cross-linking reaction (spectrum b).

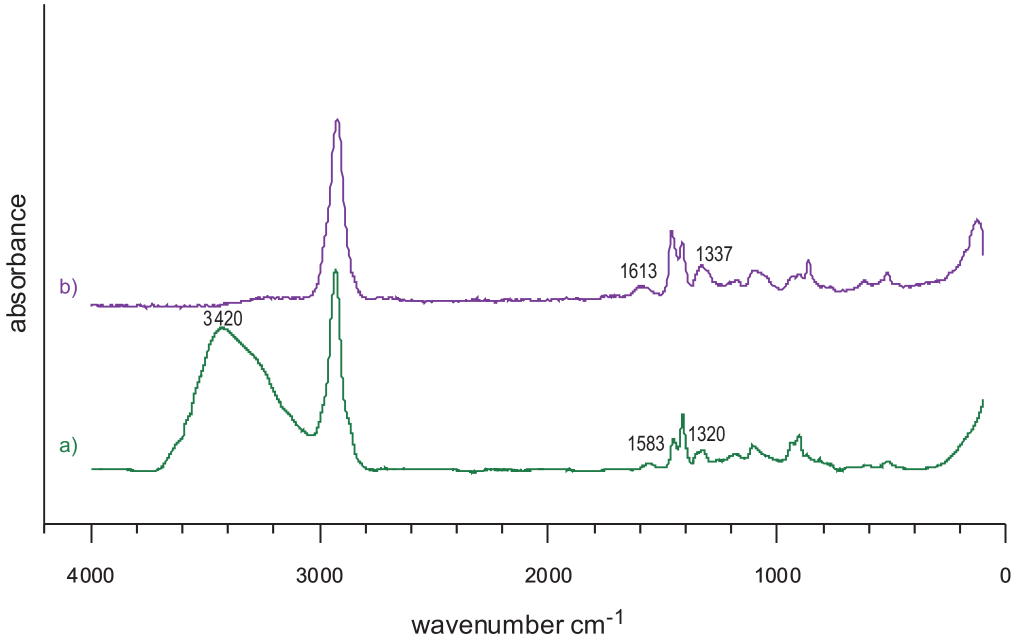


Fig. 8. Changes in the Raman spectra: a) sodium polyacrylate solution, b) sodium polyacrylate solution + microwaves

NMR spectrum presented in Figure 9 exhibits a new signal at 220.92 ppm, after cross-linking done by microwaves. It can be assigned to carbon atoms appearing in ester or anhydride group. A decay of the signal originated from carbonyl group -C=O (δ=183,4) can be also observed, which indicates that this part of carbon atoms might be participating in the formation of new bonds. Signals at 45.96 ppm and 45.09 ppm belong to carbon atom C_α, while signals at 38.75 ppm, 37.28 ppm and 36 ppm to carbon atom C_β.

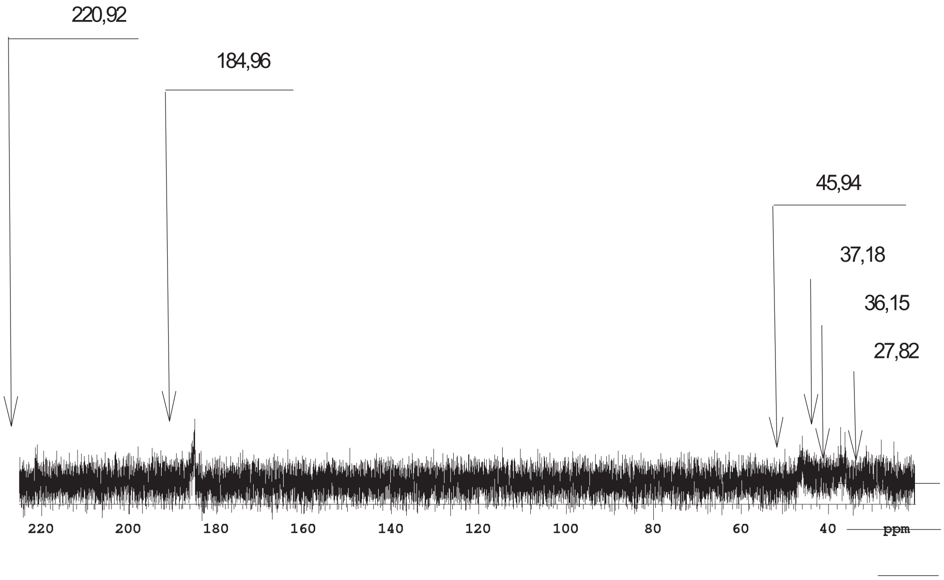


Fig. 9. ^{13}C NMR spectrum of sodium polyacrylate solution in D_2O + microwaves

6. Structure analysis of samples cross-linked photochemically by the UV radiation

Investigations of structure analysis concerning a time-history of the cross-linking reaction of sodium polyacrylate under the influence of the UV radiation were carried on. FT-IR spectra of sodium polyacrylate within the range of 4000-400 cm^{-1} are presented in Figure 10. In the range of wave numbers 3700-2900 cm^{-1} a certain decrease of the absorption band corresponding to stretching vibrations of -OH groups can be observed. It is caused by water evaporation. However, after the cross-linking procedure this band becomes also visible due to the presence of hydrogen bonds.

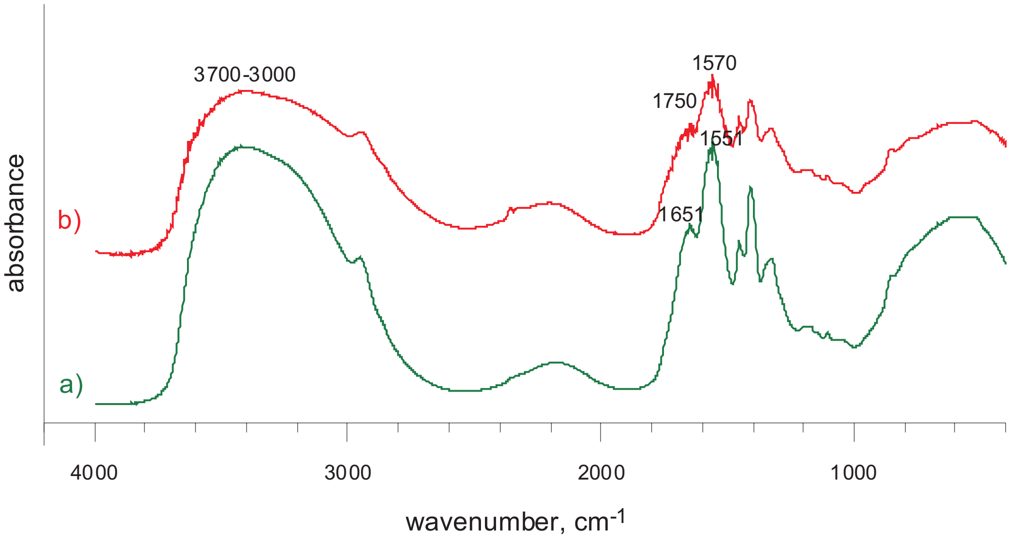


Fig. 10. FT-IR spectra: a) sodium polyacrylate solution, b) sodium polyacrylate solution + UV

The absorption band of sodium polyacrylate solution at 1551 cm^{-1}, corresponding to deformation vibrations of -C-O-H, shifts – during cross-linking caused by the UV radiation – towards higher wave numbers, namely 1570 cm^{-1}, while the band at 1651 cm^{-1} becomes smeared and shifted with an additional appearance of a wide smeared band near 1750 cm^{-1}. This band does not have any distinct maximum. Those changes can be a result of overlapping of vibrations of new carbonyl bonds of aldehyde or ketone type related to a fragmentation of polymer chains during photo-cross-linking as well as to the presence of anhydride groups.

The Raman spectra performed for sodium polyacrylate before and after cross-linking by the UV radiation in the range of 4000 100 cm^{-1} are presented in Figure 11.

Changes related to shifting the absorption band from 3420 cm^{-1} to 3275 cm^{-1} can be seen on the Raman spectra. Intensities and position changes of the band, after hardening, can be attributed to water evaporation and to vibrations of hydrogen bonds of O-H...O=C type, appearing during cross-linking reactions.

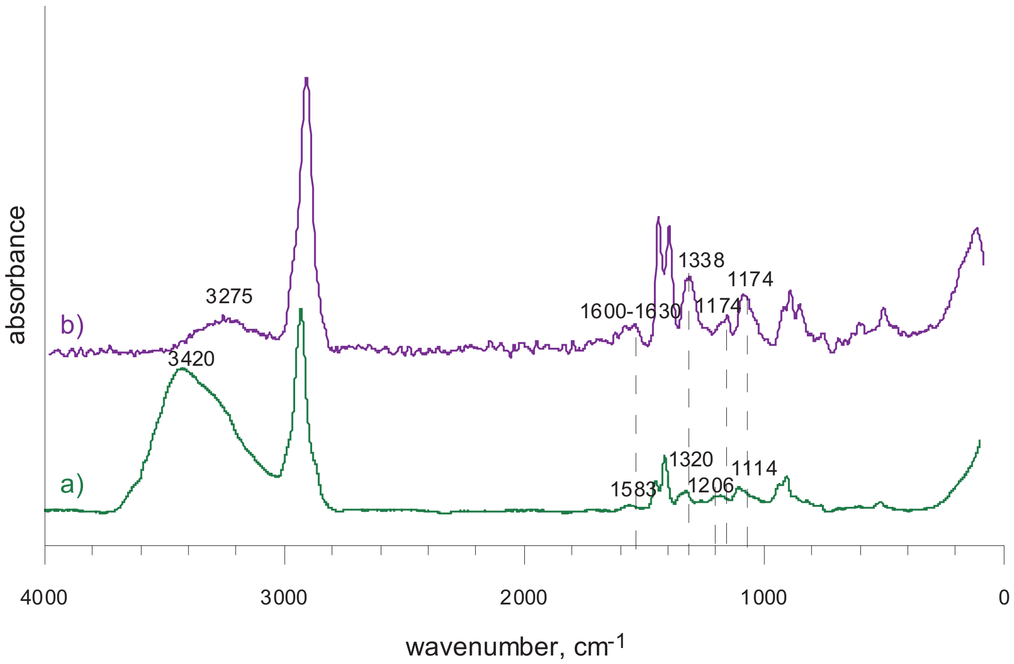


Fig. 11. Raman spectra: a) sodium polyacrylate solution, b) sodium polyacrylate solution + initiator + UV

The absorption band at 1583 cm^{-1} undergoes – during cross-linking by UV – splitting into bands at 1600 cm^{-1} and 1566 cm^{-1}. Additionally a new band at 1630 cm^{-1} is formed. It can be assumed that those shifts are related to overlapping vibrations of new bonds formed during the cross-linking reaction with the participation of carbonyl groups (of aldehyde, ketone or anhydride type). Bands shifting and wave number changes: 1320 $cm^{-1} \rightarrow 1338\ cm^{-1}$, 1206 $cm^{-1} \rightarrow 1174\ cm^{-1}$ can also indicate that COO^{-} group participates in the formation of new groups.

7. Mechanisms of the cross-linking reaction of sodium polyacrylate

During the cross-linking reaction by means of $Ca(OH)_2$ and CO_2 divalent Ca^{2+} cations are building-in into a polymer chain in place of monovalent Na^{+} cations (Fig. 12), which means it is done by bridging. Ions replacements are accompanied by conformation changes in the polymer structure, which has been confirmed by the spectroscopic examinations. Thus, the cross-linked component is formed as the result of the reaction of carboxyl and carboxylate polymer group with metal cations in a water medium [7, 12, 13]. This is an ionic reaction.

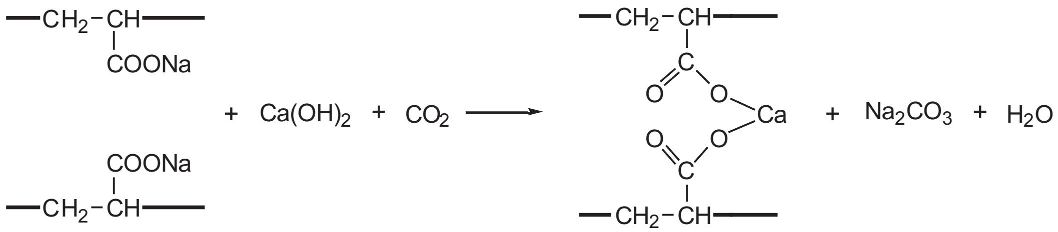


Fig. 12. Reaction of chemical cross-linking between polymer chains

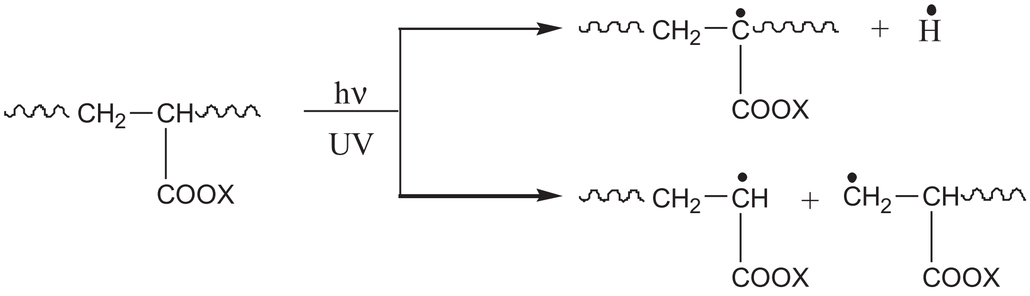
During microwaves action an alternating electric field of a high frequency is interchanging into heat emitting into the examined material. Contrary to other kinds of electromagnetic waves, the microwave radiation causes only molecule rotations in an alternating electric field without disturbing the stability of chemical bonding since the energy transferred by this type of radiation is much lower than the chemical bond dissociation energy. Interactions of the microwave radiation with the matter are done mainly by the reorientation of charged particles or being polar systems in a high frequency electromagnetic field. Active centres are created in polymer particles due to microwave actions, where an increase of reactivity followed by cross-linking reactions in between polymer chains with the participation of carboxyl and carboxylate groups - seems very important [7, 12, 13].

Microwave actions lead to a formation of new intermolecular hydrogen bonds both between polymer chains themselves and between polymer chains and water (O-H···O-H and O-H···O=C).

Additionally microwaves generate an increase of a sample temperature, causing a dehydration reaction between two carboxyl groups belonging to adjacent chains. Strong covalent bonds are being formed in this reaction.

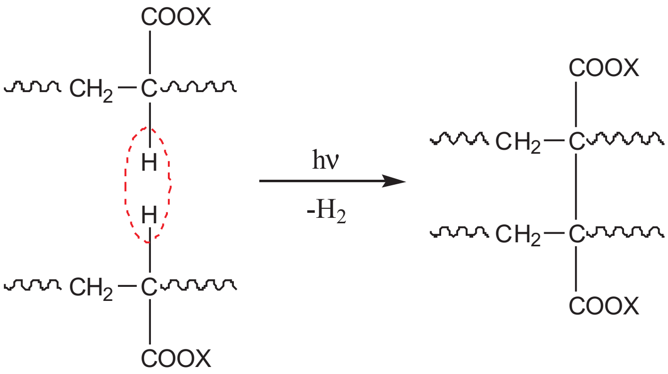
The dehydration reaction is presented below:

The cross-linking reaction of sodium polyacrylate under the influence of the UV radiation occurs with a formation of several intermediate products – active radicals, which can react with each other, what in consequence leads to the cross-linked product of a complicated structure. In addition – under these conditions – polyacrylate undergo a statistic breaking of macromolecule chains in which chain fragments of various length are formed. Energy corresponding to the UV radiation of a wave length 254 nm is satisfactory to chemical bonds C-C or C-H cleavage in examined polymers, but is not sufficient to ionise macromolecules. Therefore a majority of photochemical reactions in polymers is of a radical character. On the basis of the literature data [1, 3, 7, 12, 14] and the performed examinations the following general schemes of mechanisms of polyacrylate cross-linking reactions (with the participation of the UV radiation) – can be proposed (reaction I):

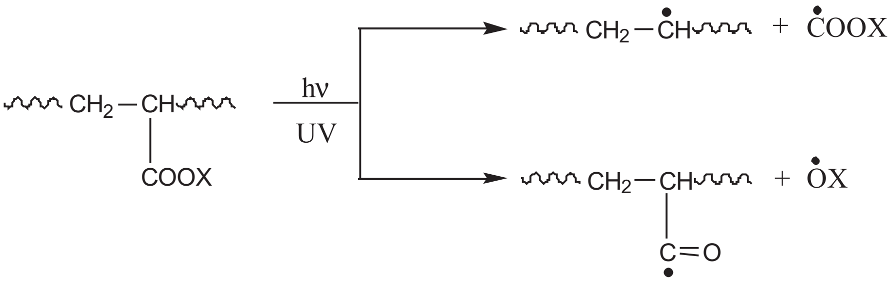


where X means either H or Na atom

Polyacrylates undergo an effective cross-linking also due to the presence of a mobile hydrogen atom at the tertiary carbon atom (reaction II):



Apart the above mentioned processes, reactions of detachment and destruction of side substituents can occur in polyacrylate being radiated (reaction III):



The formed radicals are extremely active and can easily detach hydrogen atoms from adjacent mers as well as can react with atmospheric oxygen. This leads to the formation of new bonds: ketone in the main chain or aldehyde at the macromolecule ends. In addition, the active radicals reacting with each other form branched macromolecules of quite complicated structure. The proposed schemes of the cross-linking reactions under the UV radiation influence are confirmed by the presence of characteristic absorption bands corresponding to hydrogen, anhydride, aldehyde and ketone bonds in FT-IR and the Raman spectra, obtained for the examined sodium polyacrylate. The possible products of the cross-linking reaction done by the UV radiation - with new aldehyde and ketone groups are presented in Figure 13.

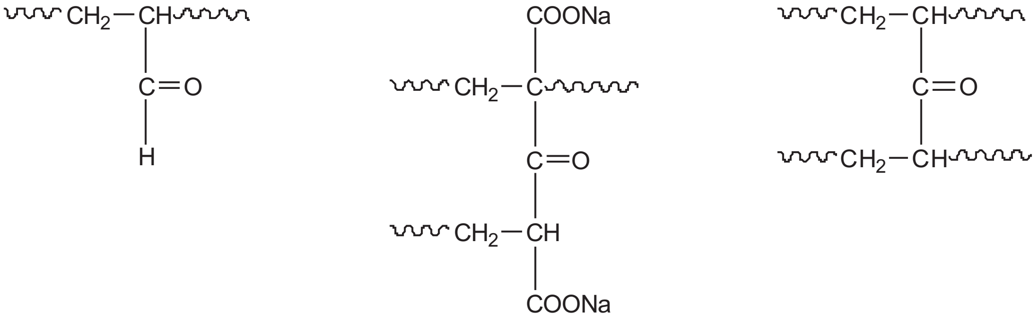


Fig. 13. Products of polyacrylate cross-linking by the UV radiation

8. Conclusions

Phenomena occurring during polyacrylate cross-linking reactions strongly depend on the applied method. Thus, the knowledge of the mechanism of binding agents bonding applied in moulding sands allows for their modification, in a way which will contribute to an improvement of physical, chemical and technological properties and to decrease environment hazards.

It has been shown – on the basis of structure examinations – that the cross-linking reaction of sodium polyacrylate by means of $Ca(OH)_2 + CO_2$ is of a ionic character. On the other hand the cross-linking reaction done by means of the microwave actions is mainly related to dehydration and to formation of inter-chain anhydride covalent bonds. The cross-linking process performed by the UV radiation is done by radicals.

Models of cross-linking mechanisms of the polyacrylic binding agent – proposed in the hereby paper – constitute fully modern approach to the hardening process of moulding sands with organic binding agents. Performing this type of structure examinations at the atomic level, with the application of the most advanced research methods, should allow to design and to manage properly technological processes.

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