



MAREK MARCISZ*, ALEKSANDER SOBOLEWSKI**

Chlorine content in bituminous coal of „Pniówek” deposit from SW part of Upper Silesian Coal Basin¹

Introduction

Chlorine, despite its low content in coal (from trace up to 1%; mean value below 0.2%), is the next element, after sulphur and nitrogen, which has a detrimental effect on natural environment in coal processing (Makowska et al. 2012; Marcisz 2013, 2014; Sablik 1998; Świetlik 2000).

Generally the content of chlorine in bituminous coal depends on grade of salinity of orogen and deposit water and coal rank. Chlorine in coal occurs in the form of chloride ions (in water bonded with coal) as well as inorganic chlorides – anhydrous (e.g. halite) and hydrated (bishofite and carnallite). In Polish bituminous coal, the element mostly occurs as NaCl halite (Sablik 1998; Makowska et al. 2012).

Under the influence of high temperature, the chlorine is transferred to coking products, constituting a detrimental impurity (Diessel 1992; Gabzdyl 1987; Mielecki 1972; Stach et al. 1982; Taylor et al. 1998).

* Dr hab. inż., Politechnika Śląska, Wydział Górnictwa i Geologii, Instytut Geologii Stosowanej, Gliwice, Poland; e-mail: marek.marcisz@polsl.pl

** Dr inż., Instytut Chemicznej Przeróbki Węgla, Zabrze, Poland

¹ Artykuł jest częścią wyników uzyskanych w ramach projektu badawczego nr POIG.01.01.02-24-017/08 pt.: „Inteligentna koksownia spełniająca wymagania najlepszej dostępnej techniki”, Etap 5.1: Zintegrowany system rozpoznania i oceny przydatności technologicznej węgla oparty na prognostycznym modelowaniu jakości otrzymywanego koksu, prowadzonym przez Instytut Chemicznej Przeróbki Węgla w Zabrzu.

The character of connection between chlorine and sodium determines form and temperature when chlorine is released from coal during its thermal processing (pyrolysis, gasification, combustion). In case of weak connection (when chlorine ion is attached to the coal surface) chlorine in the duration of pyrolysis releases in the form of HCl already by relatively low temperatures, ca. 300°C.

Anhydrous chlorides in the high temperatures (higher than their melting point e.g. for halite 801–804°C) may evaporate, but the significant evaporation of chlorine minerals can be expected already in the temperature >1400°C (in the temperature <1000°C evaporation of chlorides has marginal significance).

Hydrated chlorides undergo in the heating process complicated transformations e.g. dehydration (100–200°C), thermal hydrolysis (200–270°C) or dehydroxylation (450–575°C) occurring during pyrolysis of bischofite (Sablik 1998; Makowska et al. 2012).

The coking coal from JSW S.A. coal mines, which is the basic national raw material for the production of blast-furnace coke, is characterized by high content of chlorine ranging from 0.07 to 0.22% of Cl^a (www.jsw.pl). The coke used in modern blast furnaces which utilize large amounts of coal dust is required to have chlorine content below 0.06% (Karcz 2002). The increasingly strict requirements concerning the chlorine content, even below 0.05%, call for actions directed at the optimization of the coke production process, which is based on wet quenching, to allow for the production of coke fulfilling the quality requirements. Wet quenching of coke using water with high content of chlorides may cause that the amount of chlorine introduced to the coke from quenching water may constitute even up to 50% of its total content (Figa et al. 2006). Apart from the detrimental influence of chlorine from the coking point of view, the content is also meaningful for ecology. This is because the management and disposal of coal mining wastes has an impact on the significant increase of Cl⁻ concentration in the region of disposal, as in all types of disposed wastes, the portion of chloride is the largest – from 30 to 50% (Grabowska and Sowa 1999; Sowa 2008).

The most popular methods for the determination of chlorine in solid fuels should be the method of potentiometric titration (this method was used to determine chlorine content in coal samples which are the subject of this work). New methods of determination of chlorine are ion chromatography and elementary analysis. All three methods have similar performance characteristics (an important issue in choosing an analytical method can be played by the cost of a single analysis, its duration and easiness of its execution; Makowska et al. 2012).

The research project named “Smart coke plant fulfilling requirements of best available techniques” (IK – Inteligentna Koksownia – Smart Coke Plant) conducted since 2008 within the Innovative Economy Operational Programme has provided new data concerning the changes in chlorine content in the coal seams of the “Pniówek” deposit. The project allowed for the verification of the state-of-the-art knowledge in relation to the chlorine content variation characteristics in the deposit (Proberz et al. 2011, 2012a, 2012b).

1. Method

The paper covers results of 1136 samples analyses (furrow samples and samples obtained from boreholes), incorporated in the “Pniówek” coal mine archive, when unfortunately there are no data concerning forms of occurrence of chlorine in coal. The results were prepared and verified within the IK research project. As a result, a digital database concerning the coal quality in the range of the “Pniówek” mining area was created (Marcisz 2010b, 2013, 2014; Probiez et al. 2011, 2012a, 2012b). The analysis of the database resulted in the information that 472 samples with Cl^a chlorine identified are available for the study area. The 31.08.2009 version of the database served as a basis, but the database is updated on a current basis along with the increase of the sample population.

Within the project, 11 coal seams have been examined for Cl^a content and variation. The seams represent the Ruda, Załęże and Orzesze beds, that is the 400 and 300 group seams (Namurian C – Westphalian B). In the first stage of the research, basic statistical analyses were performed. Among other things, the number of samples from individual seams, in which the content of chlorine content was identified, was determined – as well as the minimal, maximal and mean content of the parameter in a given seam. It was counted also coefficient of variation for the chlorine content in each analyzed seams and it was given its evaluation in Baryszew scale. Next, horizontal (E-W and N-S directions) and vertical (with depth, Fig. 1) variation of the chlorine content was presented. The horizontal (lateral) directions of the chlorine content variation, reflect the general parameters of deposition

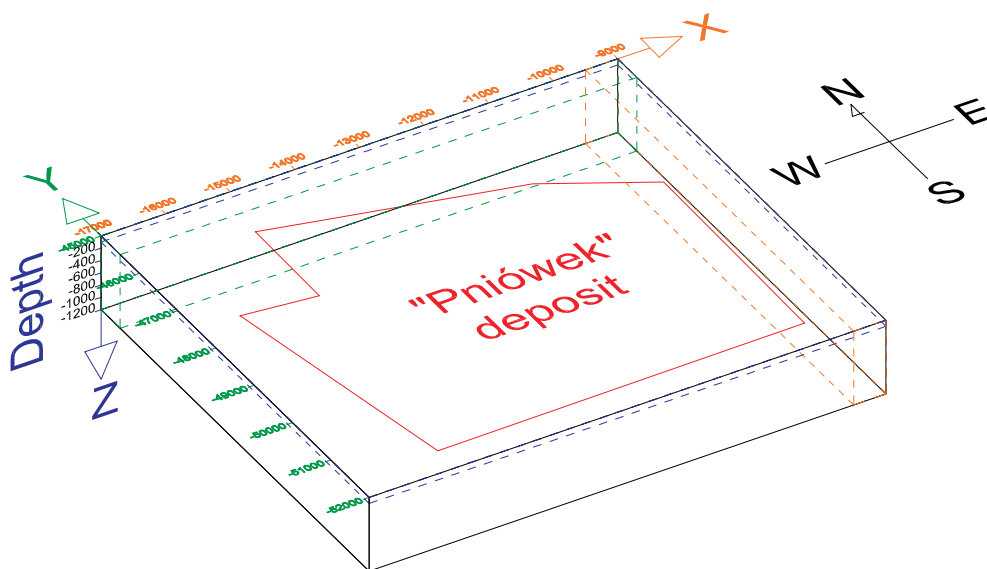


Fig. 1. Analysis diagram of chlorine content in the “Pniówek” deposit in vertical and horizontal directions

Rys. 1. Schemat analizy zmian zawartości chloru w kierunku wertykalnym i horyzontalnym w złożu „Pniówek”

in the “Pniówek” deposit: the strike (E-W) and the dip (N-S). The final stage encompassed the plotting of isoline maps of the chlorine content in all the examined coal seams. This was achieved using the Surfer program (developed by Golden Software), declaring the interpolation method in the form of radial basis functions. The distance between the gridding nodes was assumed to be 50 m – in line with the recommendations for the Upper Silesian bituminous coal (Marcisz 2010a; Proberz and Marcisz 2010, 2011).

2. Results

The statistical analysis of the created digital database concerning the “Pniówek” deposit coal quality has indicated that among all 1136 samples, chlorine identification was performed for 472 samples, which is 42% of the total population. The number of samples per the examined seams varies from 4 (p. 407/4) to 82 (p. 361, Fig. 2, Table 1).

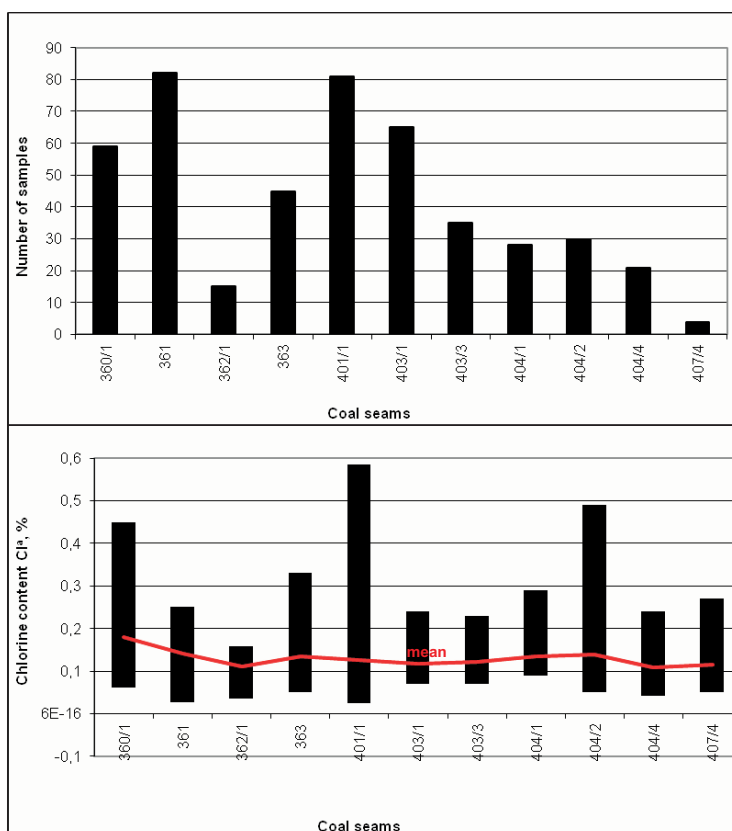


Fig. 2. Number of samples and the chlorine content (in % mass.) in the examined seams of the “Pniówek” deposit

Rys. 2. Liczba próbek oraz zakres zawartości chloru (w % wag.) w badanych pokładach węgla złoża „Pniówek”

Table 1. No. of samples and the chlorine content (in % mass.) range in the examined seams of the “Pniówek” deposit

Tabela 1. Liczba próbek oraz zakres zawartości chloru (w % wag.) w badanych pokładach węgla złoża „Pniówek”

Parameter	Coal seam					
	360/1	361	362/1	363	401/1	403/1
Number of samples	59	82	15	45	81	65
Minimum	0.062	0.026	0.035	0.050	0.025	0.070
Maximum	0.450	0.250	0.158	0.330	0.584	0.240
Mean	0.180	0.142	0.110	0.134	0.125	0.118
Standard deviation	0.057	0.037	0.033	0.046	0.066	0.034
Coefficient of variation	32	26	30	34	53	29
Deposit variation group/variation after Baryszew classification	II/average	II/average	II/average	II/average	III/large	II/average
Parameter	Coal seam					
	403/3	404/1	404/2	404/4	407/4	“Pniówek” deposit
Number of samples	35	28	30	21	4	472
Minimum	0.070	0.090	0.050	0.041	0.050	0.025
Maximum	0.230	0.290	0.490	0.240	0.270	0.584
Mean	0.121	0.134	0.139	0.109	0.115	0.134
Standard deviation	0.031	0.046	0.083	0.039	0.104	0.054
Coefficient of variation	26	34	60	36	91	40
Deposit variation group/variation after Baryszew classification	II/average	II/average	III/large	II/average	III/large	II/average

The chlorine content in the “Pniówek” deposit varies in a wide range from 0.025 to 0.584% of Cl^a content. Such a range of values provides a mean value of 0.134% of Cl^a (Table 1). The extreme values (the highest and the lowest) of this parameter have been found in the 401/1 seam, which is characterized by a mean part of Cl^a amounting to 0.125%. As far as the mean value is concerned, only the seams for which the amount of samples was higher than 30 were analyzed. As such, the lowest content of chlorine, that is 0.118% of Cl^a was found in the 403/1 seam, while the highest content, that is 0.180% of Cl^a was identified in the 360/1 seam.

The coefficient of variation counted for the deposit „Pniówek” counts 40%, what according to Baryszew classification allows to count them (considering chlorine content) to the II group of variability of deposit, i.e. deposits of average variability. To the same group of variability is counted the majority (eight) of examined coal seams with the exception of coal seams 401/1, 404/2 and 407/4, which were counted to the higher – III group of deposit variability i.e. large variability (Table 1).

Such a high disproportion called for research on the directionality of this parameter variability (Fig. 3). This paper includes the analysis of chlorine content in horizontal (X, Y) and vertical (Z) direction with the assumed scheme, as presented in Fig. 1.

The “result cloud” which might be observed in Fig. 3 does not allow for unequivocal determination of chlorine content variation tendency/directionality in the “Pniówek” deposit.

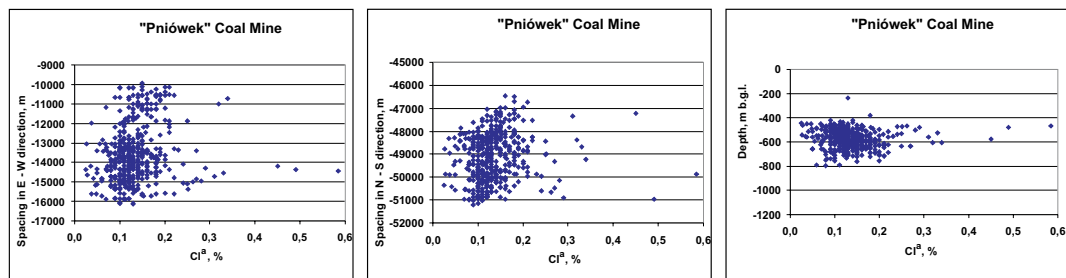


Fig. 3. Horizontal and vertical variation of chlorine content in the “Pniówek” deposit
X direction: E(–9 000) – W(–20 000); Y direction: N(–45 000) – S(–53 000);
according to the local „Sucha Góra” coordinate system – see Fig. 1

Rys. 3. Zmiany zawartości chloru w złożu „Pniówek” w ujęciu horyzontalnym i wertykalnym
kierunek X: E(–9 000) – W(–20 000); kierunek Y: N(–45 000) – S(–53 000);
według lokalnego systemu współrzędnych „Sucha Góra” – jak na rys. 1

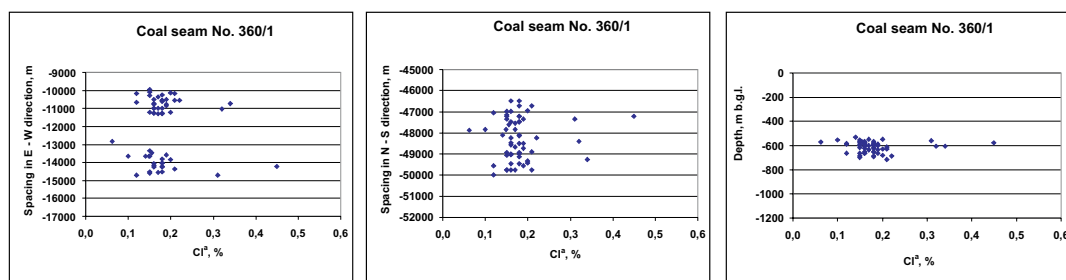


Fig. 4. Horizontal and vertical variation of chlorine content in the examined seams
Explanation as for Fig. 3. There are presented only coal seams where the amount of samples where
the chlorine was measured was larger than 30

Rys. 4. Zmiany zawartości chloru badanych pokładach w ujęciu horyzontalnym i wertykalnym
Objaśnienia jak na rys. 3. Przedstawiono jedynie pokłady węgla, gdzie liczba próbek,
w których oznaczono zawartość chloru, była większa od 30

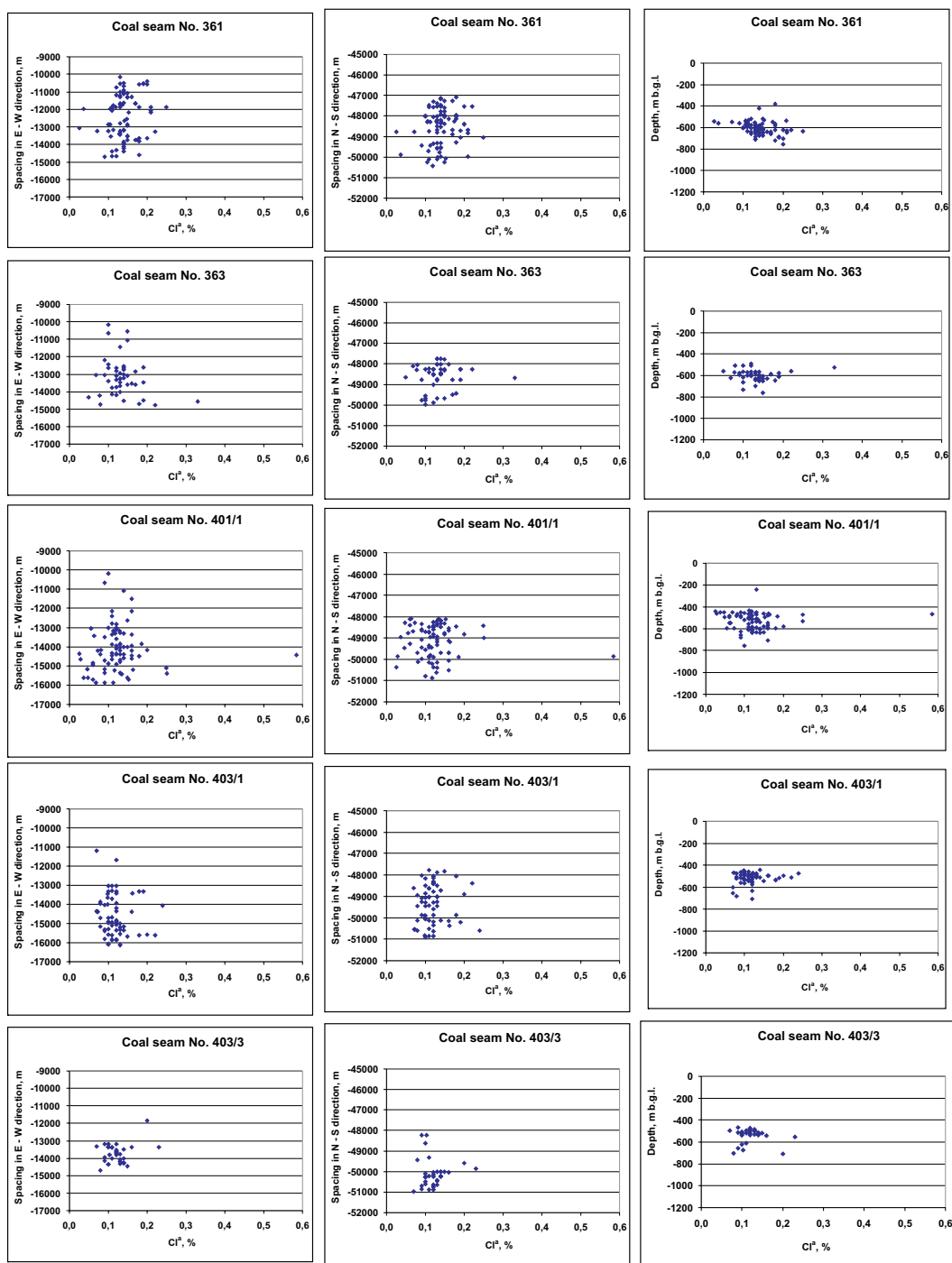


Fig. 4. cont.

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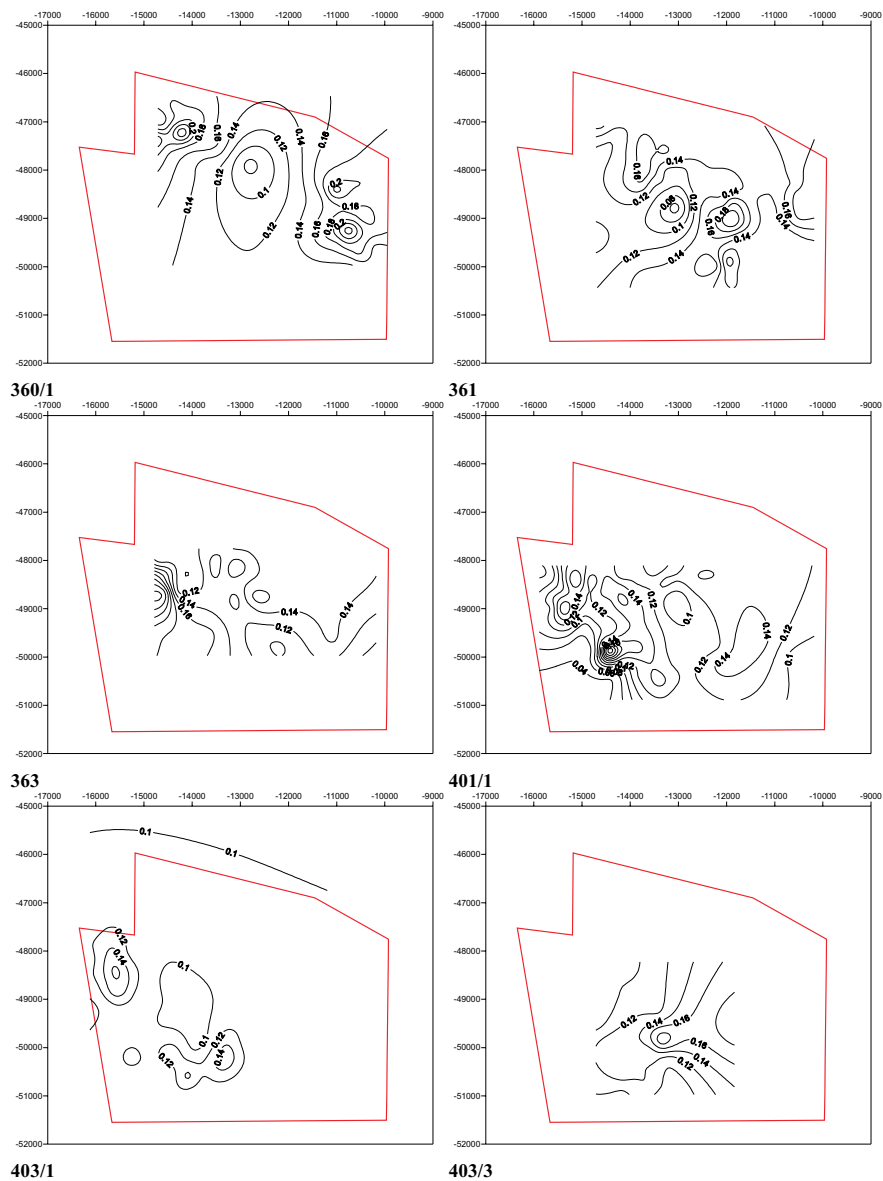


Fig. 5. The maps of interpolation values distribution of Cl_a in the examined seams, plotted using the radial basis function method

To maintain the legibility of the drawings, the locations in which the samples with identified chlorine content have been obtained have not been plotted. There are presented only coal seams where the amount of samples where the chlorine was measured was larger than 30

Rys. 5. Mapy rozkładów wartości interpolacyjnych Cl_a w badanych pokładach, wykreślone metodą Radial Basis Function

W celu zachowania czytelności rysunku nie naniesiono na mapy lokalizacji miejsc pobrania próbek, w których dokonano oznaczenia zawartości chloru. Przedstawiono jedynie pokłady węgla, gdzie liczba próbek, w których oznaczono zawartość chloru, była większa od 30

Generally it may be assumed, majority of the results of the element identification is lower than 0.15% of Cl^a.

The above findings formed a basis for an analogous analysis of the chlorine content in individual coal seams (Fig. 4) which, when combined – form the picture visible in Fig. 3.

While considering all the examined seams, no general tendency of chlorine content variation has been found either. A different pattern of variation is observed in each of the seams.

The lack of directionality in the horizontal direction referred to earlier formed a basis for the plotting of contouring maps of the content of this element in the study area (Fig. 5).

The plotted maps did not help in picturing the general tendency of chlorine content and have accentuated the assertion that in each of the seams, the variability in the distribution of the element is different. It may, however be observed, as it seems, that the chlorine content increases in the east and north-east directions. The course of the isolines also allowed to indicate the local extreme values (minimum, maximum) as well as to determine the anisotropy of the variability – density of isolines in certain directions may indicate an increased variability in these directions (Niec 1982). The maps have also allowed to draw attention to disproportions in the size of the field of observation, which is dependent both on the number of samples and their distribution. It may be expected that with the increase of the amount of data (increase of number of samples where the chlorine content will be determined) the course of isolines on the maps will change, enabling more precise showing tendencies (orientation) of changes of this element in particular coal seams.

Conclusion

The results of the research have indicated that the chlorine content in the examined seams of the “Pniówek” deposit varies in the range from 0.025 to 0.584% of Cl^a (mean value of 0.134%). The extreme (highest and lowest) values of this parameter have been found in the 401/1 seam with a mean part of 0.125% of Cl^a. No general tendency of chlorine content variation has been found. Each of the seams presents different characteristics of these variations. As it seems, it may nevertheless be observed that the chlorine content increases in the eastern and north-eastern direction. At this stage of the research (due to the insufficient number of samples and field of observation), a broader explanation of this fact is not possible.

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**ZAWARTOŚĆ CHLORU W WĘGLU KAMIENNYM ZŁOŻA „PNIÓWEK”
Z SW CZĘŚCI GÓRNOŚLĄSKIEGO ZAGŁĘBIA WĘGLOWEGO**

Słowa kluczowe

Górnośląskie Zagłębie Węglowe, węgiel kamienny, szacowanie jakości węgla,
parametry jakościowe, zawartość chloru

Streszczenie

Scharakteryzowano zmiany zawartości chloru w 11 pokładach węgla kamiennego złoża „Pniówek”. Dokonano tego na podstawie utworzonej cyfrowej bazy danych obejmującej 1136 próbek, spośród których w 472 oznaczono zawartość tego pierwiastka. Przeprowadzono podstawowe analizy statystyczne, za pomocą których określono m.in. liczbę próbek, w których oznaczono zawartość chloru w poszczególnych pokładach, a także minimalną, maksymalną oraz średnią zawartość tego pierwiastka w danym pokładzie. Prześledzono zmiany zawartości chloru w układzie horyzontalnym (w dwóch kierunkach: wschód-zachód oraz północ-południe) i wertykalnym (wraz z głębokością). Wykreślono także mapy izolinii zawartości chloru we wszystkich badanych pokładach węgla. Wyniki badań wykazały, iż zawartość chloru w badanych pokładach złoża „Pniówek” zmienia się w szerokim zakresie od 0,025 do 0,584% Cl^a (śr. 0,134%). Ekstremalne (najniższa i najwyższa) wartości tego parametru stwierdzono w pokładzie 401/1, charakteryzującym się średnim udziałem 0,125% Cl^a. Nie wykazano żadnej ogólnej tendencji zmian zawartości chloru. W każdym z pokładów obserwuje się odmienny charakter tych zmian. Można jednakże zauważyć wzrost zawartości chloru w kierunku wschodnim i północno-wschodnim.

**CHLORINE CONTENT IN BITUMINOUS COAL OF „PNIÓWEK” DEPOSIT FROM SW PART
OF UPPER SILESIA COAL BASIN**

Key words

Upper Silesian Coal Basin, bituminous coal, coal quality estimation, quality parameters,
chlorine content

Abstract

Chlorine content variability analysis has been performed for 11 coal seams of the “Pniówek” deposit. The analysis has been performed based upon a digital database including 1136 samples, among which, for 472 samples the content of this parameter was determined. Basic statistical analyses were performed, which led to the determination of the number of samples from individual seams, in which the chlorine content was specified as well as the identification of the maximal and mean content of the parameter in a given seam. The horizontal (E-W and N-S directions) and vertical (with depth) variation of the chlorine content was determined. Also isoline maps of chlorine content in all examined seams were plotted. The results have shown that the chlorine content in the examined seams of the

“Pniówek” deposit varies in a wide range from 0.025 to 0.584% Cl^a (mean of 0.134%). The extreme values (the highest and the lowest) of this parameter have been found in the 401/1 seam, which is characterized by a mean part of Cl^a amounting to 0.125%. No general tendency of chlorine content variation has been found. Each of the seams presents different characteristics of these variations. As it seems, it may nevertheless be observed that the chlorine content increases in the eastern and north-eastern direction.