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THERMAL NEUTRON ABSORPTION CROSS SECTION OF INDUSTRY BRINES

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ABSTRACT

Many procedures used for calibration of neutron porosity well-logging tools require knowledge of the thermal neutron absorption cross section of borehole brines. Results of measurements of the thermal neutron absorption cross sections of model potassium-polymer brines and of real industry potassium brines are discussed in the paper. Borehole brines are frequently assumed NaCl water solutions. The obtained experimental data show significant differences between the measured and assumed values. The measured values cover the range from 23 c.u. to 37 c.u. and the differences between the measured and the approximated values reach up to 10 c.u. The experimental method used for measurements of the neutron absorption cross section of brines is suggested as a routine procedure for well-logging companies.

1. INTRODUCTION

Many procedures used for calibration of neutron well-logging tools require knowledge of integral neutron parameters for all media surrounding the neutron tool in a borehole. The neutron tool consists of a neutron source and a neutron detector. Neutrons from the source are transported through a borehole and through a drilled rock formation. The pulses that are counted by the neutron detector are interpreted *via* a calibration procedure (in general) as the formation porosity. Knowledge of the neutron parameters is a base of proper interpretation. Among other, the thermal neutron absorption cross section influences significantly a correctness of calibrating the neutron well-logging tools.

The absorption cross section of the medium depends on its elemental composition. The case of brine requires a special attention. It frequently contains different unforeseen compounds which are added depending on the drilling conditions. A typical interpretation procedure assumes that the borehole brine is a water solution of a given concentration of sodium chloride [1]. This is a very simplified model. Borehole brines, used now routinely in our drilling industry, are prepared frequently on the base of water solutions of potassium chloride. The differences between the neutron parameters of water solutions of sodium and potassium salts were presented [2] for different borehole conditions (temperature, pressure).

The elemental composition of real brine differs significantly from the pure water solution of mentioned salts. From a few years the Polish drilling companies use potassium-polymer brines to drill shally-sandstone formations. The brines contain [3] cellulose-type (POLOFIX LV) or starch-type (ROTOCEL S) protective colloids, the encapsulating polymer (STABPOL S) and as the structure-making medium the biopolymer (XCD). There are additional compounds as KOH, K_2CO_3, potassium lignite (ARAGONIT P), potassium lignosulfate, potassium polyacrylate, carbomethoxy-cellulose potassium salt (KMC), potassium acetate and formate and potassium bromide. All these additional compounds change the absorption cross section of the brine in comparison to the pure water solution of sodium or calcium chloride.

The paper presents the measurement results of the thermal neutron absorption cross section $\Sigma_{a(exper)}$ for a series of the model polymer-potassium brines and for a series of the real industry brines. The results of the measurements for the model brines have been reported in the review paper [2] on potassium brines. Here more detailed

experimental results are reported. The experimental results are compared to the calculated $\Sigma_{a(calc)}$ values. They have been calculated as for pure salts solutions and evaluated from an approximate knowledge of brine components.

2. DESCRIPTION OF THE BRINE SAMPLES

Two series of brine samples have been used in the experiments. The first series consists of the samples prepared in laboratory conditions (in the Oil and Gas Mining Institute, Kraków, Poland) as the brine models. The compositions of these samples have been formally known (Table 1). All the components (except water and potassium chloride) are various polymer additional ingredients, specified only by commercial names. The elemental compositions of these substances are registered.

TABLE 1. Composition of the model brine samples [2].

Name tag	H_2O	KCl	MODI-CIDE 340	ROKA-CET S	BENTO-POL	STAB-POL S	POLO-FIX LV	XCD	ROKO-POL 3095	ROKA-CET R26
	dm^3	%	%	%	%	%	%	%	%	%
CZK08	1	3	0.1				2	0.2	3	1
CZK09	1	3	0.2	3				0.2	3	1
CZK10	1	3	0.2			0.2	2	0.2		
CZK11	1	3	0.2				2	0.2		
CZK12	1	3	0.2	3		0.2		0.2		
CZK13	1	3	0.2	3				0.2		
CZK14	0.97	3	0.1		3	0.2	2			
CZK15	0.97	3	0.1		3		2			
CZK16	0.97	3	0.2	3	3	0.2				
CZK17	0.97	3	0.2	3	3					

The second part of the brine samples has been taken from industry boreholes from the Southern Poland. In a few cases the same brine has been taken twice: first it was a “fresh” brine and second the same brine after a few (or more) days of use (the “used” brine). This was done in order to check whether the Σ_a of the brine changes in time of use. The compositions of these samples are presented in Table 2. It is visible that the information on the brine compositions is incomplete.

TABLE 2. Composition of the industry brine samples.

Borehole/brine information	Component	%
CZK02 Borehole: RUDKA-10	H_2O	85.
	Bentonite	4.
	KCl	3.50
	Polymers	0.28
	DEFPOL	0.1
	NaOH	0.1
	BIOSTAT	0.2
	BLOK M25	7.
	X-DRILL	2.5
CZK03 Borehole; WĘGLÓWKA-324 Potassium-polymer brine Depth: 1087 m	H_2O	78.
	Bentonite	7.8
	KCl	3.50
	Polymers	0.39
	POLOFIX LV	2.
	$BaSO_4$	6.
	DEFPOL	0.1
	NaOH	0.1
	BIOSTAT	0.2
	CON-TONE (asphalt medium)	~1.
CZK04 Borehole: NOSÓWKA-13 Potassium-polymer brine Depth: 2010 m	H_2O	78.
	Bentonite	8.55
	Polymers	0.28
CZK05 Borehole: GAWRZYŁOWA-3 Polymer brine Depth: 1000 m	H_2O	85.
	Polymers	2.8
CZK06 Borehole: OSOBNICA-143	NaOH	0.2
	BIOSTAT	0.2
	POLOFIX LV	1.5-2.0
	KCl	5.0-6.0
	$C_8H_{17}OH$	0.1-0.2
	MODISTAB	0.2-0.3
CZK07 Borehole: DŁUGOSZ-120	POLOFIX LV	2.20
	POLOFIX HV	0.10
	KCl	5.50
	Lignosulfate	0.56
	STOKOPOL	0.16
	NaOH	0.27
	DESCO	0.028
	$BaSO_4$	6.81
	$C_8H_{17}OH$	0.44
	CH_2O	0.13
	$CaSO_4.2H_2O$	0.56
	$NaHCO_3$	0.85
	Na_2CO_3	0.14
	$Ca(OH)_2$	0.14
	BIOSTAT	0.11
	BLOK 0.2	2.27

3. MEASUREMENTS OF THE ABSORPTION CROSS SECTION OF BRINES

Thermal neutron absorption cross section Σ_a has been measured using a pulsed neutron source method on the experimental set-up at the pulsed neutron generator [4]. The simplified Czubek's method has been used [5]. The absorption rate $\langle \upsilon \Sigma_a \rangle$ of the measured sample is the primary result of the experiment, where υ is the thermal neutron speed. The optimal range of absorption rates which can be measured on the existing experimental setup is 12000 s^{-1} < $\langle \upsilon \Sigma_a \rangle$ < 25000 s^{-1}. Absorption rate for water and water solutions of KCl up to 10 % cover the range 5000 s^{-1} < $\langle \upsilon \Sigma_a \rangle$ < 11500 s^{-1} (Table 3). This means that absorption rates of the investigated brine samples have $\langle \upsilon \Sigma_a \rangle$ close to the minimum value of the optimal range. Preliminary experiments made on all the samples confirmed that presumption.

The following procedure has been used to perform the measurements. The brine samples have been poisoned by water solutions of defined H_3BO_3 concentrations. The thermal neutron absorption cross section of brine sample has been calculated from the data:

$\langle \upsilon \Sigma_a \rangle$ measured mean value of the absorption rate of a poisoned sample, [s^{-1}]

υ thermal neutron speed, [cm s^{-1}]

V volume of the poisoned sample, [cm^3]

m_b, m_k mass of the brine sample and of the water solution of H_3BO_3, [g],

ρ_b density of the brine sample, [g cm^{-3}]

Σ_{ak}^M mass absorption cross section of the water solution of H_3BO_3, [cm^2 g^{-1}]

The 2% water solution of H_3BO_3 has been used in the experiments. The mass absorption cross section of the boric acid used was:

$$\Sigma_a^M (100\%\ H_3BO_3) = 7.6258 \pm 0.0195\ cm^2\ g^{-1}$$

which gives:

$$\Sigma_{ak}^M (2\%\ H_3BO_3) = 0.1744 \pm 0.0004\ cm^2\ g^{-1}$$

The absorption cross section of the brine sample is then given by:

$$\Sigma_{a(exper)} = \rho_b \left[\frac{V}{m_b} \frac{\langle \upsilon \Sigma_a \rangle}{\upsilon_0} - \frac{m_k}{m_b} \Sigma_{ak}^M \right], \qquad (1)$$

where the neutron speed υ_0 = 220 000 cm s^{-1}.

The experimental results $\Sigma_{a(exper)}$ are collected in Table 4 for the series of model brines and in Table 5 for the industrial brines.

4. ATTEMPT TO CALCULATE Σ_a OF THE BRINE SAMPLES

The thermal neutron macroscopic absorption cross section of a homogeneous mixture of *J* chemical compounds can be calculated from the formula [6]:

$$\Sigma_a = \rho N_A \sum_{j=1}^{J} \left[\sum_{i=1}^{I} \frac{\sigma_i n_{ij}}{M_j} \right] q_j \qquad (2)$$

where ρ is density of the mixture; N_A is the Avogadro's number; σ_i is the microscopic absorption cross section of the *i*–th element; n_{ij} is the number of atoms of the *i*–th element in the stoichiometric formula of the *j*–th compound; M_j is the gram molecule in the *j*-th compound; q_j is the weight content of the *j*–th compound in the mixture.

The formula (2) has been used to calculate Σ_a for the brine samples under the assumption that the absorption cross section for all the compounds with unknown chemical formulae is equal to zero. The absorption cross sections of H_2O, KCl, NaOH, $BaSO_4$, $C_8H_{17}OH$, CH_2O, $CaSO_4$, $NaHCO_3$, Na_2CO_3, $Ca(OH)_2$ and of bentonite have been taken in proportions as shown in Table 2. The absorption cross section of bentonite has been calculated from the formula for the typical montmorylonite: Al_2O_3(16.5%) + Fe_2O_3(2.5%) + MgO(6.5%) + CaO(2.15%) + SiO_2(54.35%) + H_2O(18%). Using that procedure we should obtain the lowest limit of $\Sigma_{a(calc)}$ for brine samples. The experimental results are then expected to give higher values.

The second possibility is to assume that the absorption cross sections of the brine samples correspond to pure water solutions of given concentrations of KCl. Table 3 contains the neutron absorption parameters and densities for water solutions of KCl at 20 °C. It can be expected that such calculations give values $\Sigma_{a(calc)}$ higher than measured cross sections. It is caused by a high absorption of chlorine which dominate other elements. This statement may be false when the brine contains boron.

TABLE 3. Neutron absorption parameters and density of water solutions of KCl at 20 °C.

Concentration	Density	$\langle \upsilon \Sigma_a \rangle$	$\Sigma_a(\upsilon_0)$	Concentration	Density	$\langle \upsilon \Sigma_a \rangle$	$\Sigma_a(\upsilon_0)$
[%]	[g cm^{-3}]	[s^{-1}]	[c.u.]	[%]	[g cm^{-3}]	[s^{-1}]	[c.u.]
0	0.998	4893	22.24				
1	1.005	5477	25.01	11	1.070	12106	55.04
2	1.011	6121	27.85	12	1.077	12849	58.24
3	1.017	6777	30.73	13	1.084	13480	61.48
4	1.024	7373	33.63	14	1.091	14241	64.77
5	1.030	8046	36.59	15	1.098	15013	68.09
6	1.037	8731	39.57	16	1.105	15655	71.45
7	1.043	9338	42.58	17	1.112	16446	74.86
8	1.050	10041	45.65	18	1.119	17248	78.31
9	1.057	10755	48.73	19	1.126	18061	81.80
10	1.063	11374	51.86	20	1.133	18721	85.33

The measured and calculated absorption cross sections for the series of model brines (listed in Table 1) are presented in Table 4. The measured values are in the range 29 c.u. $< \Sigma_{a(exper)} <$ 32 c.u., and the standard deviation is about 1 c.u. The calculated values differ from the measured ones no more than 2 c.u. All the samples in that series contain 3 % of KCl. The absorption cross section of the 3 % KCl water solution is equal Σ_a(3%KCl) = 30.73 c.u. A worse situation is observed when the measured values are compared to the absorption cross section of 3 % NaCl water solution, Σ_a(3%NaCl) = 32.64 c.u.

TABLE 4. Measured and calculated absorption cross sections for the series of the model brines listed in Table 1. (Based on [2]).

Name tag	Density ρ_b	$\Sigma_{a(calc)}$ $\sigma(\Sigma_{a(calc)})$	$\Sigma_{a(exper)}$ $\sigma(\Sigma_{a(exper)})$	Name tag	Density ρ_b	$\Sigma_{a(calc)}$ $\sigma(\Sigma_{a(calc)})$	$\Sigma_{a(exper)}$ $\sigma(\Sigma_{a(exper)})$
	g cm^{-3}	c.u.	c.u.		g cm^{-3}	c.u.	c.u.
CZK08	1.03	29.12 0.08	30.57 1.01	CZK13	1.03	30.06 0.09	29.00 1.63
CZK09	1.03	28.86 0.08	28.99 0.90	CZK14	1.05	29.91 0.08	32.06 0.71
CZK10	1.03	30.24 0.09	30.57 1.04	CZK15	1.05	29.97 0.08	31.91 1.05
CZK11	1.03	30.28 0.09	32.08 1.33	CZK16	1.05	29.66 0.08	30.54 1.65
CZK12	1.03	30.01 0.09	29.58 1.99	CZK17	1.04	29.42 0.08	30.39 0.79

Concluding, one can say that polymer additives to the potassium brines can change the absorption cross section up to 3 c.u. It is comparable with a change of the

KCl concentration from 3 % to 3.5 %. Approximation of the absorption cross section of potassium-polymer brine by the absorption of a pure water solution of NaCl (with the same concentration as of KCl) is sometimes used. From the analysis performed it is obvious that such a method will give overestimated results. When the interpretation procedure requires using data of NaCl solution as a borehole brine, an equivalent NaCl concentration should be introduced calculated as shown in [1] or [2].

TABLE 5. Measured and calculated absorption cross sections for the series of the industry brines listed in Table 2.

Name tag	Density ρ_b	$\Sigma_{a(calc)}$	$\Sigma_{a(exper)}$ $\sigma(\Sigma_{a(exper)})$	Remarks	
	g cm^{-3}	c.u.	c.u.		
1	2	3	4	5	6
CZK02	1.19	34.77	30.06 0.69	3.5% KCl 32.13 c.u.	3.5% NaCl 34.41 c.u.
CZK03	1.49	41.96	29.84 0.75	as above	
CZK04	1.49	26.62	24.61 0.67	Pure water: 22.24 c.u.	
CZK05	1.25	23.64	33.11 0.79	as above	
CZK06	1.24	42.79	37.68 0.71	5.5% KCl 38.05 c.u.	5.5% NaCl 41.51 c.u.
CZK07	1.42	45.44	36.74 0.57	as above	
CZK18	1.16	------	23.33 0.92	3% KCl 30.73 c.u.	3% NaCl 32.64 c.u.
CZK19	1.16	------	24.29 0.67	as above	
CZK20	1.17	------	23.12 0.62	as above	
CZK21	1.08	------	31.20 0.44	as above	
CZK22	1.14	------	23.29 0.59	as above	
CZK23	1.19	------	24.01 0.81	as above	
CZK24	1.12	------	31.81 0.75	as above	
CZK25	1.14	------	29.53 0.98	as above	
CZK26	1.13	------	30.01 0.77	as above	

The results for the second series (industry brines, see Table 2) are presented in Table 5. The differences between the measured and calculated values of the absorption cross sections are significant. Column 5 contains the calculated values of the absorption cross section for water solution of KCl of the concentration corresponding with the contribution in the given brine. These values are also inconsistent with the measurement results. For comparison Column 6 contains the calculated values of the absorption cross sections for the respective NaCl solutions.

A conclusion is obvious: the evaluation of the absorption cross section for the industry brines on the basis of pure solutions of KCl introduces a significant error in the interpretation procedure of the neutron well-logging. The error grows when the borehole brine is approximated by NaCl solutions. Therefore, the absorption cross section of industry brines should be experimentally determined on samples.

An additional test has been done for the investigated industry brines. Three samples of the same industry brine have been taken twice: first directly after preparing the brine ("fresh" brine) and second after a few days of work ("used" brine). The comparison of the absorption cross sections measured is presented in Table 6. No differences have been observed but the number of the tested samples is too small to generalize that statement.

TABLE 6. Absorption cross section measured for fresh and used brines.

Name tag	$\Sigma_{a(exper)}$ $\sigma(\Sigma_{a(exper)})$	
	[c.u.]	
	Fresh brine	Used brine
CZK25/CZK26	29.53 0.98	30.01 0.77
CZK21/CZK24	31.20 0.44	31.81 0.75
CZK20/CZK23	23.12 0.62	24.01 0.81

4. CONCLUSIONS

The approximation of the neutron absorption cross section for potassium brines by the absorption cross section of a pure water solution of NaCl brings in to the well-logging interpretation error values in calculating the corrections for the neutron absorption in a borehole. The error grows with the concentration of the salt in the brine

[2]. In the examples presented in the paper that procedure overestimates the absorption cross section of brines. It is visible both for model and real brines. The approximation of real potassium brines by pure water solutions of KCl is better. The absorption cross sections of the brines are less overestimated because the absorption cross section of KCl is lower than of NaCl.

From the analysis of the results for real brines we recommend measuring the thermal neutron absorption cross section of the brine before performing a neutron measurements in a borehole. The experimental method, worked out for needs of the measurements described in the paper, is not too complicated and can be offered as a routine procedure for well-logging companies.

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