



## Water soluble salts in degradation processes of stony architectural monuments in the Upper Silesia

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The study goals were aimed at obtaining information on corrosion products of rocks used in architectural monuments in the Upper Silesia. Samples from four monumental buildings located at margins of the Upper Silesia were used in the study. Three of them are located in the western part of the region: a castle at Toszek, a grain elevator at Stare Gliwice and castle ruins at Chudów, and one is located in the eastern part (a castle at Będzin). Samples of rocks from area significantly less affected by atmospheric contamination (castle ruins at Mirów in the Jura Krakowsko-Częstochowska region) were analyzed for comparison. Samples of sandstone, limestone and granitoids were analyzed with X-ray diffractometry and microstructural analyses. Chemical analyses were conducted for aqueous solutions of powdered rock samples. The following compounds were detected in the studied samples: sulphates, chlorides, nitrates and carbonates. Total salinity in the samples of sandstone and limestone was calculated, based on the results of chemical analyses and X-ray diffractometry. The highest salinity was detected in the samples from the castle ruins at Chudów.

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### INTRODUCTION

Aqueous solutions of salts migrating in the stony elements of buildings significantly affect weathering processes of these structures. Corrosion mechanisms are based on physical and chemical processes, with water being their important component, dissolving and transporting salts, and occasionally their hydrolysis (S. Skibiński, 1989). Salts soluble in water are natural components of many rocks, they also form in the hazardous amounts in reactions between gaseous atmospheric pollutants and primary components of rocks. Separations within the rock structure are the most hazardous symptoms of degradation caused by dissolving salts. Presence of dissolving salts reduce rock cohesiveness and compactness, and cause loss of mechanical strength of rocks resulting from chemical decomposition of mineral components. The most noticeable symptoms of salt activity are their crystalline efflorescence on rock surfaces, which depending on salt type and quantity,

form various types of incrustations: hard and dense (i.e. calcium carbonate), fluffy (sodium sulphate) or glassy (potassium sulphate).

Rock corrosion causes increased crystallization salt pressure. Degradation results from crystal formation and growth, and from hydration and hydration pressure. Intensity of these processes, as degrading forces, is associated with salt solution concentrations, crystallographic form, salt aqueous solubility coefficient, temperature and frequency of rock wetting and drying (P. A. Baedeker *et al.*, 1992; B. O. Fobe *et al.*, 1995; R. Löfvendahl *et al.*, 1992; H. Sweewers, R. van Gricken, 1992).

### STUDY SCOPE AND METHODS

The study was conducted using samples of four monumental objects located at margins of GOP (the Upper

Table 1

List of samples analyzed using specific methods

Sample location	Lithological type	Sample symbol	Analysis scope			
			SEM microscopy	XRD	chemical analysis of aqueous solutions	
Będzin castle	limestones	51w	x			
		52w		x		
		53w		x		
		54w	x		x	
		55w				
		56w		x	x	
Chudów castle ruins	sandstones	1p		x	x	
		2p	x			
		6p	x	x		
		13p	x			
			15p	x		x
	limestones	1w	x	x	x	
		4w		x	x	
		5w		x		
		9w	x			
	granitoids	1g				
		2g		x		
		3g	x	x		
grouts	6z		x			
	7z		x			
Stare Gliwice grain elevator	quartzitic sandstones	21p			x	
		23p	x	x		
	limestones	21w				
		22w			x	
		24w		x	x	
	granite	21g		x		
Toszek castle	sandstones	11p		x		
		12p	x	x	x	
		14p	x	x		
		31p		x		
			32p	x		
	limestones	11w	x	x		
33w		x				
Mirów castle ruins	sandstones	41p		x	x	
		42p	x	x	x	
		45p	x			
	limestones	43w	x	x	x	
	grouts	42z		x		
44z			x			

w — limestones, p — sandstones, g — eratic blocks (granitoids), z — grouts

Silesian Industrial Region), three of them located in western part: a castle at Toszek, a grain elevator at Stare Gliwice and castle ruins at Chudów and one located in eastern part (a castle at Będzin). For comparison, rock samples from an object located in a region of significantly less atmospheric pollution were analyzed. Castle ruins at Mirów (Jura Krakowsko-Częstochowska) is the object.

Samples of construction rocks were collected, so that they possibly represent all lithologic types used in the studied objects. Additionally, samples of exposed and of protected, for example by vegetation (assuming that affecting processes depend on degree of wetness and rate of rock drying), wall fragments were collected. Outer layers of weathered surfaces, which cover some rocks, and grout were also sampled. Sampling of all objects was accompanied by lithological inventory of construction materials. Samples in all objects were collected at elevation of 0.5–2.0 m above the land surface. Some samples collected at Chudów were collected at elevation of 0.3 m (1w, 15p, 11g and 18g). Symbols which include sample number and lithological type were used for sample designation. Sandstone samples were designated with letters “p”, limestones as letter “w”, and eratic blocks as letter “g” (granitoids). Samples of grout were designated with letter “z”. List of analyzed samples is presented in Table 1. Because of the specificity of construction materials, in many cases, the amount of collected samples was insufficient for all planned analyses. This fact complicated interpretation of the results and caused necessity of application of analogies observed macroscopically.

Detailed identification of phase composition of rocks and coatings at external surfaces was conducted, based on the results of X-ray diffractometry. X-ray diffractometry was conducted on powdered samples. Analyses were conducted using *TUR-61/HZG-4* diffractometer, with monochromatic, Fe-filtered  $\text{CoK}\alpha$  radiation in the range of 5–35  $\Theta$ . X-ray diffraction was also used to identify the precipitates formed on glass slides by drying the extracts of soluble components of the rock samples. The XRD patterns were obtained with *GEIGERFLEX* diffractometer (*Rigaku-Denki*) using Fe-filtered  $\text{CoK}\alpha$  radiation. Phases were identified based on the reference data in Mineral Powder Diffraction File (1986) and V. I. Mikheev (1957).

Precipitates on glass slides were also examined in polarized light using *Reichert MF2* optical microscope. Scanning electron microscopy (*SEM*) with chemical analyzer was used for selected samples to characterize composition of subsurface layers. Samples were prepared as cuts both perpendicular and parallel to the external, weathered part of rock samples. Samples were carbon-coated. Samples 1w, 12p and 3g were analyzed with *ISM-5300 SEM* equipped with *LINK-ISIS* detector which allowed to identify light elements (atomic number  $Z < 8$ ). Other samples were examined with *JEOL Superprobe 733* electron microscope equipped with *JC XA 733* microprobe. Elements heavier than  $Z = 8$  were identified using energy-dispersive spectrometer. Carbon and nitrogen were analyzed with wavelength-dispersive spectrometer. Quantitative analysis of carbon was of limited precision due to carbon-coating on sample surfaces.

Qualitative chemical analyses included some of the ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ) in aqueous solutions of powdered samples. These analyses were aimed at determination of soluble substances, especially salts which are products of rock weathering.

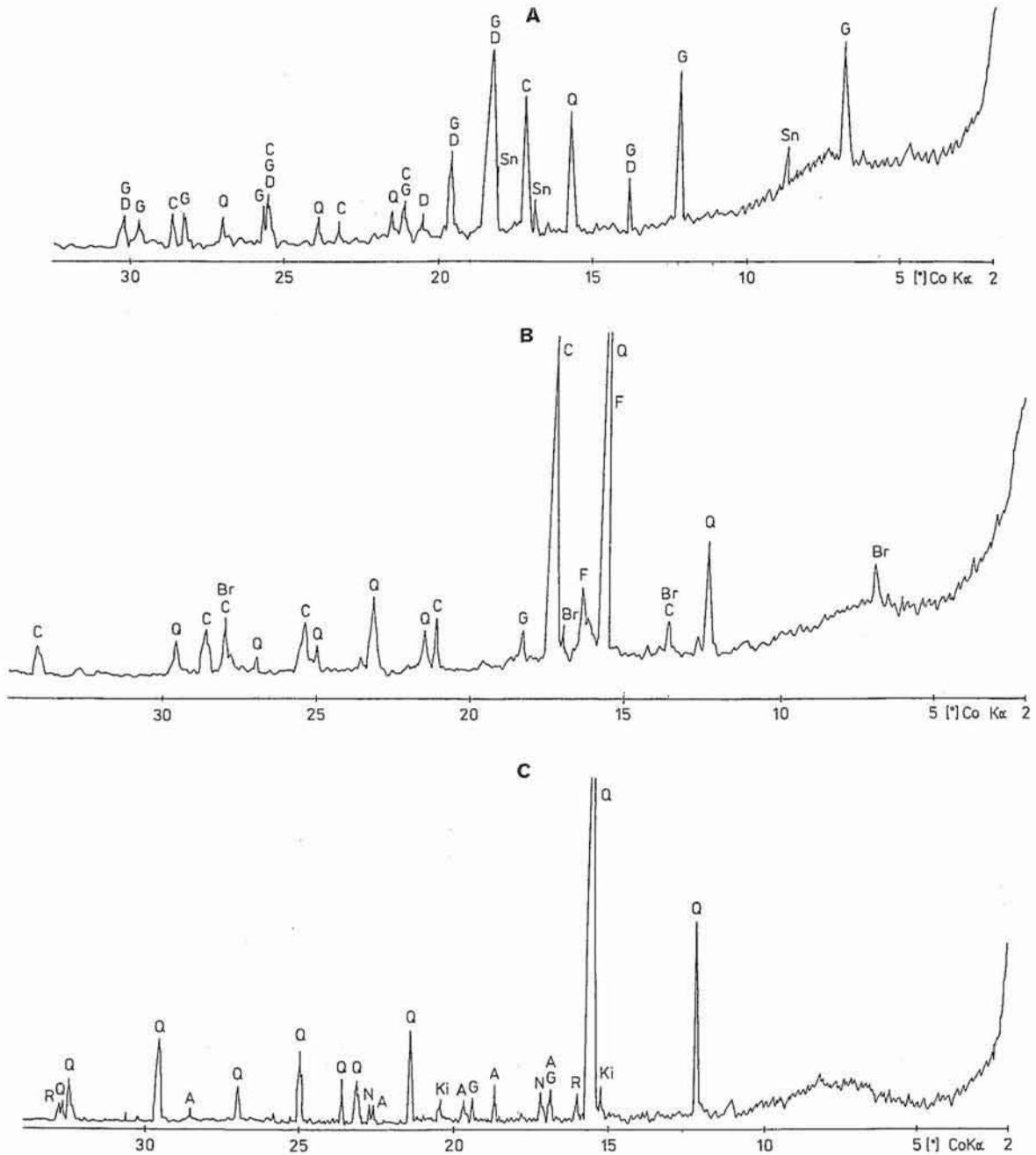


Fig. 1. XRD pattern: A — sample from a dark incrustation on dolomitic limestone (53w, Będzin castle), B — grout sample (6z, Chudów castle ruins), C — sandstone sample (14p, Toszek castle)

C — calcite, D — dolomite, G — gypsum, Q — quartz, Sn — syngenite, Br — brushite, F — frondelite, A — blodite, Ki — kieserite, N — nitronatrite, R — rutile

Dyfraktogram rentgenowski: A — próbki ciemnego naskorupienia na wapieniu dolomitycznym (53w, zamek w Będzinie), B — próbki zaprawy (6z, ruiny zamku w Chudowic), C — próbki piaskowca (14p, zamek w Toszku)

C — kalcyt, D — dolomit, G — gips, Q — kwarc, Sn — syngenit, Br — brushyt, F — frondelit, A — astrachanit, Ki — kizeryt, N — nitronatryt, R — rutil

## X-RAY DIFFRACTOMETRY

Several samples, representing various lithological types from different monumental objects, were analyzed with X-ray diffractometry. Samples of dolomitic limestones were collected in the Będzin castle. Mineral composition of a sample

of thick black incrustation on the rock surface (sample 53w) was analyzed. Following minerals were identified: dolomite, calcite, gypsum, quartz and syngenite ( $K_2SO_4 \cdot CaSO_4 \cdot H_2O$ ) (Fig. 1A). In deeper parts of a sample 56w only dolomite and calcite, and in a sample 52w — calcite, dolomite and small quantities of gypsum were identified, respectively.

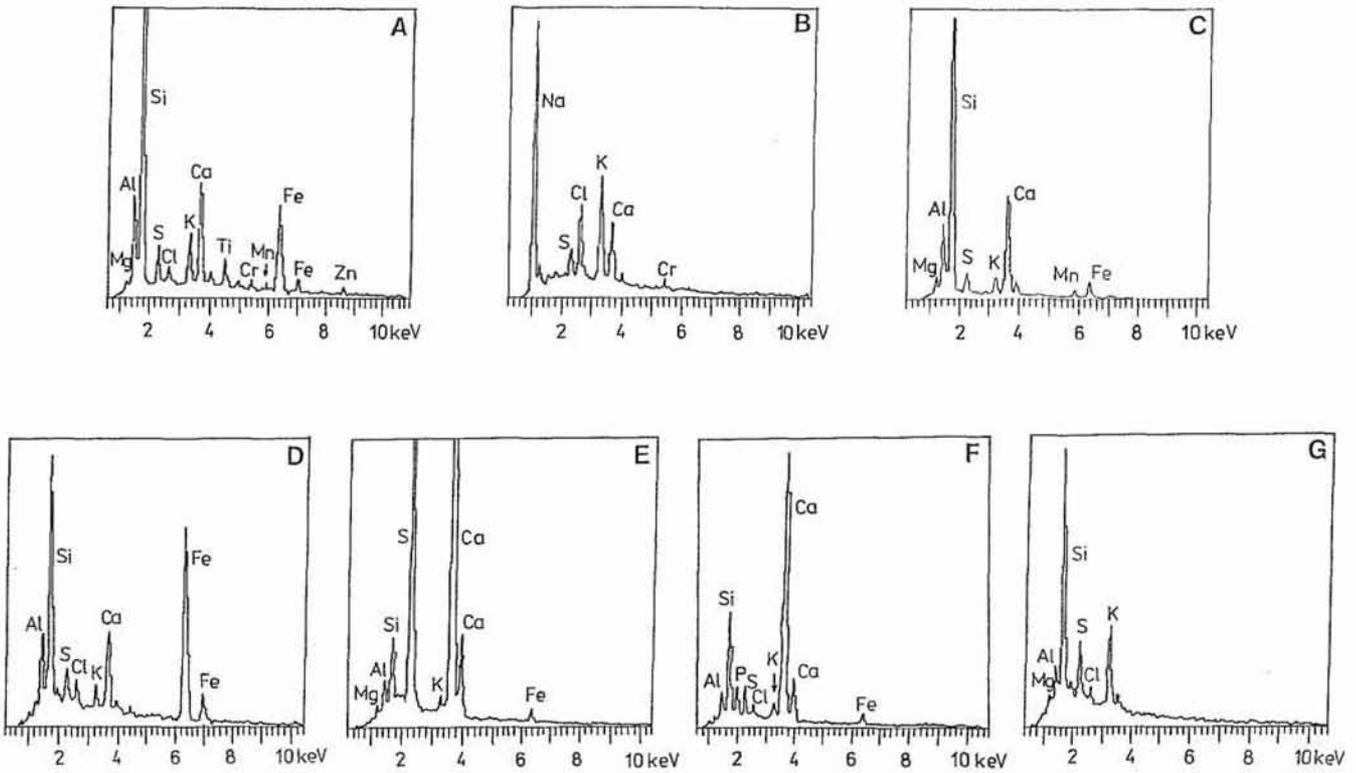


Fig. 2. Total element composition: A — dark incrustation on an external dolomitic limestone surface (54w, Będzin castle), B — external zone in a dolomitic limestone sample (54w) in a distance of 250  $\mu\text{m}$  from the surface (Będzin castle), C — polyhalite crystal  $\text{MgK}_2\text{Ca}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ , with admixtures of iron and manganese oxides in a sandstone sample (2p, Chudów castle ruins), D — incrustations on sandstone (6p, Chudów castle ruins), E — incrustations in a limestone sample (9w, Chudów castle ruins), F — external surface of limestone (11w, Toszek castle), G — surface in sandstone (45p, Mirów castle ruins)

Zbiórca skład pierwiastkowy: A — ciemnego naskorupienia na zewnętrznej powierzchni wapienia dolomitycznego (54w, zamek w Będzinie), B — zewnętrznej strefy próbki wapienia dolomitycznego (54w) w odległości 250  $\mu\text{m}$  od powierzchni (zamek w Będzinie), C — kryształu poliwalitu  $\text{MgK}_2\text{Ca}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$  wraz z domieszkami tlenków Fe i Mn w próbce piaskowca (2p, ruiny zamku w Chudowie), D — naskorupień na piaskowcu (6p, ruiny zamku w Chudowie), E — naskorupień w próbce wapienia (9w, ruiny zamku w Chudowie), F — zewnętrznej powierzchni wapienia (11w, zamek w Toszku), G — powierzchni piaskowca (45p, ruiny zamku w Mirowie)

X-ray diffractometry was used to analyze samples of sandstone, limestone, granitoids and construction grout, collected in the Chudów castle ruins. In sample 1p quartz, feldspars (mostly albite), and also illite, chlorite, gypsum and kieserite were identified. Analysis of the external strongly weathered portion of this sample indicated presence of quartz, calcite, gypsum, mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) and sylvine. In sample 6p only quartz, feldspars, clay minerals (kaolinite and illite) and gypsum were identified. In samples of limestone, in addition to their predominant component calcite, small quantities of quartz and also hanksite ( $9\text{Na}_2\text{SO}_4 \cdot 2\text{Na}_2\text{CO}_3 \cdot \text{KCl}$ ) in samples 1w and 4w, or hexahydrate in samples 5w, were identified. Composition of two granitoid samples was analyzed in samples 2g and 3g. In addition to minerals typical for these rocks (i.e. quartz and feldspars) small quantities of gypsum were detected. Calcium carbonate and quartz are major minerals of the grout used in the Chudów castle. X-ray diffractometry also indicated presence of potassium nitrate ( $\text{KNO}_3$ ) in the sample 7z, and of gypsum, brushite and frondelite in the sample 6z respectively (Fig. 1B). Presence of

brushite ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ), dicalcium phosphate dihydrate (DCPD), is associated with alteration of bones (A. Bolewski, 1982), which in this particular case may be related to old grout technology, where often not entirely burnt animal bones were added to grout. Though frondelite, an anhydrous phosphate  $\text{MnFe}_3[\text{PO}_4]_3[\text{OH}]_5$ , typically occurs with goethite in oxidation zones. Potassium in the grout sample 7z may be related to applications of charcoal in old methods of lime calcination.

The sample 23p, collected in the Stare Gliwice grain elevator, is composed entirely of quartzite and no other, than quartz, minerals were detected. X-ray diffractometry of limestone (24w) also did not indicate any contaminants or products of rock weathering (exclusively pure calcium carbonate). In a sample 21g only typical naturally occurring components of granitoids were detected.

In samples collected in the Toszek castle, in addition to naturally occurring sandstone components like quartz, feldspars, muscovite, biotite, occasionally chlorite, the following salts were identified:

- gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (incrustation in a sample 11p and in samples 12p and 14p),
- thenardite  $\text{Na}_2\text{SO}_4$  (12p),
- szomolnokite ( $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ ) (12p),
- thermonatrite  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$  (incrustation in 12p),
- hexahydrate  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  (12p),
- sylvine KCl (12p),
- kieserite  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$  (14p),
- nitronatrite  $\text{NaNO}_3$  (14p),
- blodite  $\text{Na}_2\text{Mg}[\text{SO}_4]_2 \cdot 4\text{H}_2\text{O}$  (14p).

Diffractiongram of a sandstone sample 14p is presented in Figure 1C.

Two samples of the same limestone (11w) from the Toszek castle were analyzed. In addition to calcite and gypsum, small quantities of silica were detected in one of the samples, and blodite ( $\text{Na}_2\text{Mg}[\text{SO}_4]_2 \cdot 4\text{H}_2\text{O}$ ) was detected in the other sample.

Sandstone samples collected in the Mirów castle ruins (41p and 42p) are composed mostly of quartz and small quantities of gypsum. Only one sample of limestone 34w was analyzed, which indicated only presence of natural component calcite. Additionally, two macroscopically different grout samples were analyzed. In sample 42z a greater amounts of quartz, calcite and gypsum were detected.

Within a scope of X-ray-structural analyses, composition of precipitates formed on glass slides by drying the extracts of soluble components of some rock and grout samples was determined. Results of these analyses are presented in Table 2. Precipitates, from powdered rock samples (sandstone, limestone, granite) as well as grout and brick samples on glass slides were analyzed in polarized light with *Reichert MF2* optical microscope. These samples indicate crystals of gypsum, halite, and secondarily crystallized carbonates (Pl. I and II).

Table 2

Mineral composition obtained from XRD diffractometry of precipitates formed on glass slides by drying the extract of soluble components (uncertain components given in paranthesis)

Sample symbol	Mineral composition
1p	gypsum, halite, northupite — $\text{MgCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot \text{NaCl}$
12p	kaolinite, illite (chlorite, metaaluminite — $\text{Al}_4[\text{SO}_4(\text{OH})_{10}] \cdot 5\text{H}_2\text{O}$ , fairchildite — $\text{K}_2\text{Ca}[\text{CO}_3]_2$ )
14p	illite, Mg-chamosite, muscovite
21p	gypsum, kaolinite, illite (fairchildite — $\text{K}_2\text{Ca}[\text{CO}_3]_2$ )
11ww	gypsum (traces of sulphates)
11wz	gypsum (traces of other sulphates), kaolinite, illite, smectite
43z	gypsum, calcite

ww — internal part of limestone, wz — external part of limestone; other explanations as in Table 1

## X-RAY MICRODIFFRACTOMETRY

### BĘDZIN

A dolomitic limestone sample 51w indicates plates of gypsum and dust grains composed of clay and silica. A cut perpendicular to an external surface was analyzed in a dolomitic limestone sample 54w allowed for detailed. It analysis of a dark incrustation on the sample surface which thickness approached 3–4 mm. Industrial dust, gypsum, sylvine (KCl) and grains of clay minerals were identified in the sample. Gypsum becomes a dominant component of the incrustation from a depth of 250  $\mu\text{m}$  to an interface with limestone (intercrystallized crystals of gypsum and limestone). Gypsum and

Table 3

Results of chemical analyses of aqueous solutions of sandstone samples collected from objects at Chudów, Stare Gliwice, Toszek and Mirów

Sample symbol	Cations [miliequivalents/g sample]					Anions [miliequivalents/g sample]				Deficiency anions (A)/ cations (K)
	$\text{Na}^+$	$\text{K}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	cations total	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	Cl-	anions total	
1pw	49.38	17.39	111.81	20.31	198.89	31.74	31.74	52.07	115.55	A
1pz	21.44	19.76	349.49	—	390.69	3.61	147.04	53.17	203.82	A
12pw	7.50	9.67	9.29	—	26.46	2.25	11.93	5.59	19.77	A
12pz	3.66	25.23	8.17	3.29	40.35	8.56	17.45	7.36	33.37	A
15pw	0.19	1.92	6.90	1.72	10.73	4.72	13.42	—	18.14	K
15pz	9.62	21.25	1831.61	107.28	1969.76	2.40	1288.08	—	1290.48	A
21pw	0.37	1.22	6.55	6.55	14.69	—	14.29	—	14.29	A
21pz	0.62	2.23	16.87	4.60	24.32	—	14.76	—	14.76	A
41pw	—	0.08	6.10	—	6.18	—	19.58	—	19.58	K
41pz	0.38	0.42	35.38	—	36.18	—	20.09	—	20.09	A
41pk	—	0.50	40.16	—	40.66	—	31.60	—	31.60	A
42pw	—	0.70	11.86	—	12.56	—	15.90	—	15.90	K
42pz	0.35	0.97	18.25	—	19.57	—	13.06	—	13.06	A

pw — internal part of sandstone, pz — external part of sandstone, pk — contact between sandstone and limy grout

Table 4

Results of chemical analyses of aqueous solutions of limestone samples collected from objects at Chudów, Stare Gliwice, Toszek and Mirów

Sample symbol	Cations [miliequivalents/g sample]					Anions [miliequivalents/g sample]				Deficiency anions (A)/ cations (K)
	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	cations total	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	anions total	
1ww	7.42	2.57	16.75	–	26.74	11.27	6.23	6.78	24.28	A
1wz	26.14	8.31	279.60	27.87	341.62	50.70	282.45	20.89	354.04	K
4ww	0.33	0.43	5.45	–	6.21	–	1.69	0.67	2.36	A
4wz	0.46	0.70	8.45	–	9.61	2.38	0.70	–	3.08	A
22ww	3.71	7.58	11.36	6.24	28.89	17.52	5.03	3.78	36.33	K
22wz	6.56	9.76	5.078	20.98	88.08	63.50	43.63	5.69	112.82	K
24ww	13.00	8.99	68.82	5.28	96.09	65.34	46.01	11.23	122.58	K
24wz	20.78	17.46	323.73	20.16	382.13	138.61	451.13	17.68	607.42	K
43ww	0.82	0.35	10.29	3.36	14.85	7.20	9.26	–	16.46	K
43wz	3.09	2.13	168.15	–	173.37	5.05	195.29	–	200.34	K
54ww	29.82	9.23	133.11	37.28	219.44	69.18	164.47	27.32	260.97	K
54wz	40.95	15.40	178.95	60.38	295.68	101.34	214.22	33.83	249.39	K
56ww	17.63	8.03	68.36	49.81	143.83	119.12	26.10	58.16	203.38	K
56wz	18.76	8.49	110.21	40.32	177.78	125.11	71.47	57.99	254.57	K

Explanations as in Table 2

chlorides KCl and NaCl are also present in the limestone (Figs. 2A and B).

#### CHUDÓW

Accumulations of clay minerals, products of feldspar weathering, were often observed in sandstone intergranular pores. Sandstone cement often contains significant amounts of iron oxides, though X-ray diffractometry indicates that they are accompanied by sulphur. In near-surface zones of the analyzed samples elevated concentrations of sulphur, chlorine, potassium and calcite were observed. In sample 2p local accumulations of manganese were detected. Remaining X-ray diffractometry background impulses are produced by aluminosilicates (Fig. 2C).

Incrustations characterized by elevated concentrations of iron and sulphur were found in sandstone 6p, which may indicate presence of iron sulphate ( $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ ) — szomolnokite or more often occurring  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  — melanterite (Fig. 2D). Small crystals of KCl occur in the incrustations. Additionally, small gypsum crystals are present as well. In sample 13p, except for platy accumulations of clay minerals, no other weathering products were determined. Small amount of zinc brings attention in sandstone sample 15p, which is probably related to dust contaminants.

Secondarily crystallized crystals, mostly  $\text{CaCO}_3$  and gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , are present at external surfaces of limestone samples. Results of analysis of sample 9w indicate significant amounts of sulphur and calcium (present as gypsum) and very small quantities of magnesium, potassium, and iron (Fig. 2E). Diffraction lines of the latter ones may be caused by clay minerals which cement calcite grains, or may be caused by small quantities of arcanite  $\text{K}_2\text{SO}_4$  and epsomite

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , since typical for these minerals microstalactites were detected in the microscopic analysis.

In a granite sample 3g, gypsum efflorescence was detected in fractures between crystals of quartz and feldspars. These localities enhance accumulations of dust pollutants. Similarly to other rocks X-ray pattern impulses caused by chlorine ions are present and their amplitude is related to potassium content, which might reflect the presence of sylvine.

#### STARE GLIWICE

Quartzitic sandstone (23p) is relatively less weathered. SEM pictures display a smooth external surface without coatings and efflorescence typical for secondary minerals. Some other quartz grains are slightly fractured. In deeper zones, at a distance of tens of micrometres from the surface, small quantities of clay minerals accumulate, where also elevated, in comparison to background, concentrations of iron ions were observed. In limestone (24w), similarly to sample 9w at Chudów, recrystallized calcite crystals are present in addition to small quantities of gypsum.

#### TOSZEK

Elevated amounts of sulphur, calcium, iron, sodium and potassium, as well as presence of anthropogenic dust were observed in sandstone samples from the Toszek castle walls. Surfaces of these rocks are covered with spotty, rubbing off, dusty coating. In sandstone (14p) gypsum (in significant quantities), calcium nitrate — nitrocalcite  $\text{Ca}(\text{NO}_3)_2$ , as well as sylvine KCl and halite NaCl were identified.

Large quantities of gypsum, iron oxides and hydroxides, and admixtures of KCl occur in sandstone (12p). In sample

Table 5

Content of soluble in water salts in samples of sandstones and limestones, based on the results of chemical analyses of aqueous solutions and results of X-ray-structural analyses

Sample symbol	Sulphates								Chlorides		Azotanes					Carbo-nates	Complex salts
	gypsum	thenardite	mirabilite	arcanite	szomol-nokite	kieserite	hexa-hydrate	epsomite	sylvine	halite	nitrokalite	nitro-natrite	nitro-calcite	Mg(NO <sub>3</sub> ) <sub>2</sub>	nitram-mite	thermo-natrite	hanksite
1pw 1pz	963 12 655					1420 -			1485 1686	1726 1254		1700 -	963 296				
12pw 12pz	986 704	134 260			- 175		- 377		365 482		227 865					270 -	
15pw 15pz	593 98 384		28 1547	195 2161	60 -	121 7440							- 197				
21pw 21pz	525 629	26 44		105 192					484 573								
41pw 41pz 41pk	526 1668 2977	- 27 -		7 36 43													
42pw 42pz	1021 1011	- 33		61 85	283 -												
1ww 1wz	250 19 719				- 924	- 1695			180 567	244 733			338 4158				288 1135
4ww 4wz	137 61								32 -	13 -	- 72	- 40	- 99				9 -
22ww 22wz	7 86								4 10		9 12	5 13	- 13	7 36	14 43		
24ww 24wz	39 110	12 6			- 26	6 6	or 9 or 9	or 10 or 10	10 5	2 -			48 -			32 44	
43ww 43wz	3 146	- 0.7			- 16	1.4 -	or 2.4 -	or 2.7			0.2 3	0.4 2	2 -			0.5 -	
54ww 54wz	164 255	12 32				19 9	or 32 or 15	or 35 or 17	10 21	15 13				20 65			
56ww 56wz	24 159				chloromagnezite	16 38	or bishofite	35 81	7 16	11 28			38 82	15 19	50 175		

Explanations as in Tables 2 and 3

Table 6

Total salinity in sandstones and limestones — based on the Table 5

Sample location	Litological type	Sample number	Salinity [%]
Będzin castle	dolomitic limestones	54ww	0.02
		54wz	0.04
		56ww	0.02
		56wz	0.06
Chudów castle ruins	sandstones	1pw	0.83
		1pz	1.59
		15pw	0.10
		15pz	10.97
	limestones	1ww	0.14
		1wz	2.89
Stare Gliwice grain elevator	quartzitic sandstones	21pw	0.11
		21pz	0.14
	limestones	22ww	< 0.01
		22wz	0.02
		24ww	0.01
		24wz	0.02
Toszek castle	sandstones	12pw	0.20
		12pz	0.28
Mirów castle ruins	sandstones	41pw	0.05
		41pz	0.17
		41pk	0.30
	limestones	42pw	0.14
		42pz	0.11
		43ww	< 0.01
43wz	0.02		

Explanations as in Tables 2 and 3

32p significant accumulations of gypsum plates and sporadic occurrence of barium were observed.

Composition of a limestone (11w) external surface (Fig. 2F) indicates occurrence of silicon and aluminum ions, which results from the presence of clay minerals on the sample surface; phosphorus is probably associated with naturally occurring apatite in carbonate rocks. In this sample smaller, than in other carbonate rocks analyzed, amounts of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  accompanied by relatively large amounts of sylvine were indicated by SEM microscopy.

#### MIRÓW

In sandstone sample 42p, in addition to naturally occurring rock components (quartz and iron oxides and hydroxides), only very small quantities of gypsum were identified. Larger concentrations of sulphur ions, not associated with the presence of calcium, occur in sample 45p (Fig. 2G). Potassium and magnesium sulphates may occur in sample as well. Potassium may partly react with a chlorine ion. In some places, stalactite-type dripforms composed of calcium carbo-

nate were observed. A dark coating is present on a surface of the limestone sample 43w. X-ray diffractometry mostly indicated presence of gypsum, as well as iron compounds and silica grains.

#### RESULTS OF CHEMICAL ANALYSES

Samples of analyzed sandstones and limestones were prepared from two zones: external (pz and wz designations) and internal (pw and ww designations). Chemical composition of a contact between a sandstone and a limy grout (pk designation) was analyzed in the sample 41p. Concentrations of soluble in water substances were measured in aqueous extracts from powdered rock samples. Results of chemical analyses of aqueous extracts from the samples described above are presented in Tables 3 and 4.

Sulphates, nitrates and chlorides are present in aqueous solutions obtained from rock samples, which indicates presence of soluble in water salts. Deficiency of anions, caused by the absence of analysis of a carbonate ion  $\text{CO}_3^{2-}$ , typically occur in sandstone samples. Predominant cation deficiency in limestones was supplemented by ammonium  $\text{NH}_4^+$  and iron  $\text{Fe}^{2+}$  ions.

#### RECAPITULATION

Based on comparison between obtained results with results of X-ray diffractometry, a list of soluble in water salts which may occur in analyzed rock samples was prepared (Table 5). Qualitative composition of soluble in water salts in analyzed samples was estimated, based on chemical analyses and comparison with results of X-ray structural analysis and microstructural analysis, in cases where they were available. It should be noticed that many of the substances listed in the table may be subjected to hydration or dehydration, depending on external conditions. Particularly szomolnokite ( $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ ), as a mineral typically occurring in dry conditions may be easily hydrated, which produces tetrahydrate plagonite or heptahydrate melanterite. Degree of salt hydration depends not only on a season but also on short-term weather fluctuations. Sample preparation procedures also affect degree of hydration. Total salinities (expressed as weight %) of analyzed sandstones and limestones are presented in Table 6, and were calculated as sum of soluble in water salts, presented in Table 5.

In external, near-surface zones of the analyzed samples, total salinity is significantly higher (Table 6). Only in a sandstone sample 42p from Mirów, the opposite tendency was observed but relative differences between salinities are small. In sample 41p, a grout contact zone is characterized by higher salinity than that of the external zone in the same sample. It indicates intensive chemical reactions in this zone. Products of these reactions remain in rocks; they are not easily leach-

able as they are in the external part. Based on the study results, clastic rocks (sandstones) are presumably characterized by higher salinity than in carbonate rocks. Only an external zone limestone at Chudów 1w indicates very high salinity and particularly high gypsum content. The highest total salinity was measured in rocks from the Chudów castle ruins, particularly the external zone of sandstone sample 15p. Significantly higher than in a sample 1p, salinity in this case may result from a fact that sample 15p was collected at lower elevation above the ground surface (ca. 30 cm); sample 1p was collected at elevation ca. 80 cm. Similar tendency occurs between limestone samples 1w and 4w, although difference in salinity is here significantly smaller. Observation presented above indicates that some salts might originate from soils.

Considering an assumption used in stony materials preservation that 1% by weight content of all salts in a material is the maximum allowable salinity (P. Stępień *et al.*, 1993), it should be concluded that rock samples from the Chudów castle ruins are characterized by excessive salinity. It refers to

external zones of samples 15p (10.97%), 1p (1.59%) and 1w (2.89%).

Based on the study results it appears that magnitude of atmospheric, industrial and transport related pollution does not affect directly degree of salinity of stony materials. Samples of rocks collected in the Mirów castle ruins, despite its location in relatively less industrialized region, do not reflect lower values of salinity than these measured in samples from the Będzin castle walls. It partly results from the fact that few-millimetre thick, gypsum-salt coatings form on dolomitic limestone surfaces in Będzin, where soluble substances precipitate from migrating in fractures solutions. Thus in rock itself, amounts of soluble in water salts is relatively small.

Based on the comparison of total salinity in analyzed samples, it may be concluded that amount of soluble in water salts is mostly dependent on lithological type, and in a much lesser degree on magnitude of atmospheric pollution.

*Translated by Marek Matyjasik*

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## SOLE ROZPUSZCZALNE W WODZIE W PROCESACH NISZCZENIA KAMIENNYCH ZABYTKÓW BUDOWLANYCH NA GÓRNYM ŚLĄSKU

### Streszczenie

Jednym z najistotniejszych czynników wpływających na przebieg i intensywność wietrzenia kamiennego budulca jest siła krystalizacji soli rozpuszczalnych w wodzie. Sole takie, migrujące w skale za pośrednictwem wody porowej, powstają w wyniku naturalnego rozkładu mineralów skałotwórczych, a także w wyniku korozji kamienia spotęgowanej oddziaływaniem zanieczyszczeń atmosferycznych.

Przeanalizowano skład chemiczny stref przypowierzchniowych skał dla uzyskania informacji o produktach ich korozji. Badania przeprowadzono na próbkach skał, będących budulcem czterech obiektów zabytkowych znajdujących się na obrzeżeniach Górnośląskiego Okręgu Przemysłowego: trzech w części zachodniej (zamek w Toszku, spichlerz w Starych Gliwicach i ruiny zamku w Chudowie) oraz jednego w części wschodniej (zamek w Będzinie). Porównawczo przebadano ponadto próbki pochodzące z ruin zamku w Mirowie (Jura Krakowsko-Częstochowska) zlokalizowanego w regionie o znacznie mniejszym stopniu zanieczyszczenia atmosferycznego. Z

wymienionych obiektów pobrano próbki piaskowców, wapieni i granitoidów, a w niektórych przypadkach również próbki zaprawy murarskiej i cegieł (tab. 1).

Badania rentgenowskie wykazały, oprócz typowych składników mineralnych, obecność siarczanów, azotanów, chlorków i soli złożonych (fig. 1, tab. 2). Mikroanalizy rentgenowskie wykazują w przypowierzchniowych partiach badanych próbek podwyższone zawartości siarki, chloru i żelaza. W ciemnych naskorupieniach, występujących głównie na powierzchniach wapieni dolomitycznych pochodzących z zamku w Będzinie, występują pyły przemysłowe, gips, chlorki i minerały ilaste (fig. 2, tabl. I i II).

Analizy chemiczne objęły oznaczenia ilościowe niektórych jonów ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ) w roztworach wodnych uzyskanych ze sproszkowanych próbek skał (tab. 3 i 4).

Porównując uzyskane wyniki z rezultatami analiz rentgenowskich, zestawiono wykaz soli rozpuszczalnych w wodzie, jakie mogą występować w

badanych próbkach skał (tab. 5). W strefach przypowierzchniowych badanych skał zasolenie sumaryczne jest wyższe (tab. 6). Stopień zasolenia skał zależy głównie od ich typu litologicznego. Najsilniejszemu wietrzeniu ulegają skały okrucowe, w mniejszym stopniu skały węglanowe; skały magmowe są najbardziej odporne. Wśród soli rozpuszczalnych w wodzie,

występujących w badanych skałach, znajdują się chlorki, siarczany, azotany i sole złożone. Notowane są one nie tylko w wykwitach i naskorupieniach, ale także w przypowierzchniowych partiach bloków skalnych. Elementy kamienne w dolnych partiach murów wykazują wyższe zasolenie sumaryczne niż pozostałe, co wskazuje na częściowe pochodzenie soli z gruntu.

## EXPLANATIONS OF PLATES

### PLATE I

Fig. 3. Crystals of gypsum and halite crystallized from incrustations in silty sandstone in the Toszek castle (parallel nicols)

Kryształy gipsu i halitu wykrystalizowane z naskorupień z piaskowców mułowcowych z zamku w Toszku (nikole skośne)

Fig. 4. Gypsum from incrustations on dolomitic limestones in the Będzin castle (crossed nicols)

Gips z naskorupień na wapieniach dolomitycznych z zamku w Będzinie (nikole skrzyżowane)

Magn. x 350

### PLATE II

Fig. 5. Crystals of gypsum crystallized from grout sample 43z in Mirów (parallel nicols)

Kryształy gipsu wykrystalizowane z próbki zaprawy 43z z Mirowa (nikole skośne)

Fig. 6. Secondary crystallized carbonates and gypsum from sediment deposited on a brick at Toszek (parallel nicols)

Wtórnie wykrystalizowane węglany i gips z osadu powstałego na cegle — Toszek (nikole skośne)

Magn. x 350

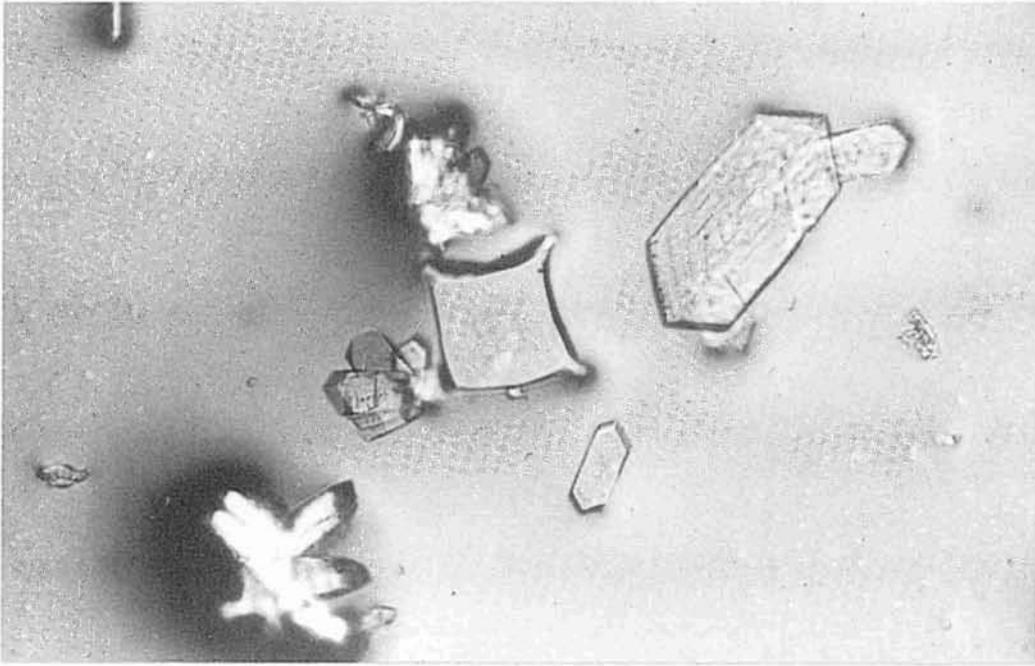


Fig. 3

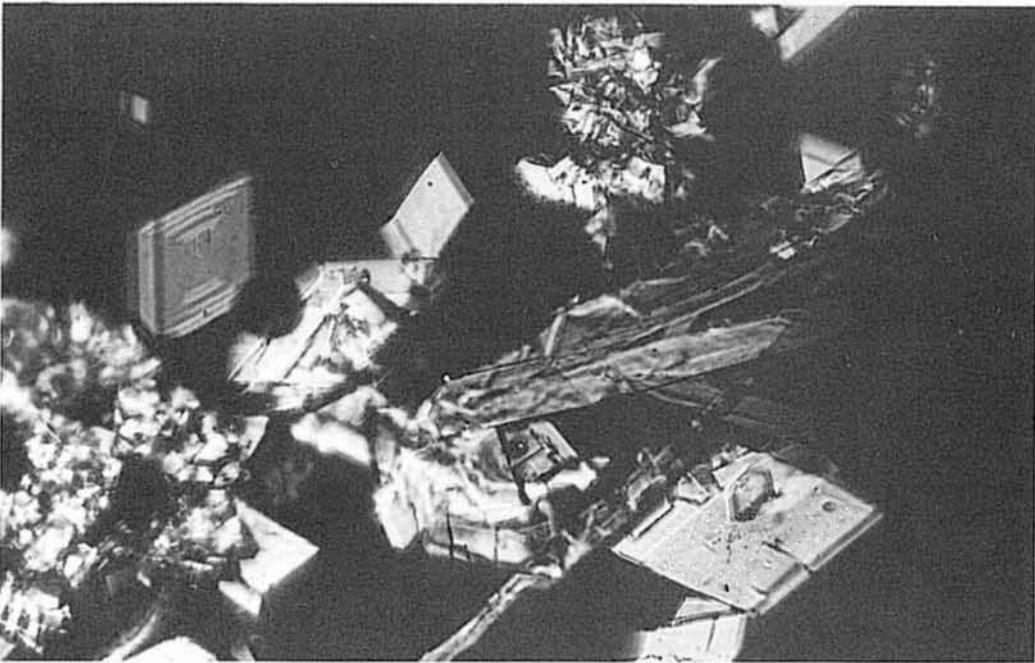


Fig. 4

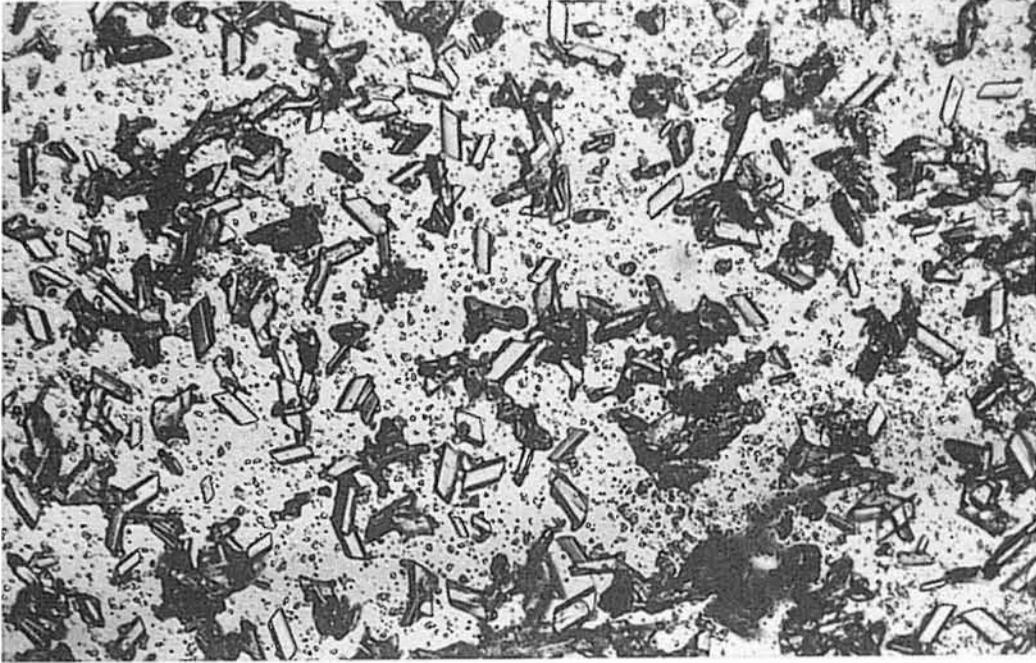


Fig. 5

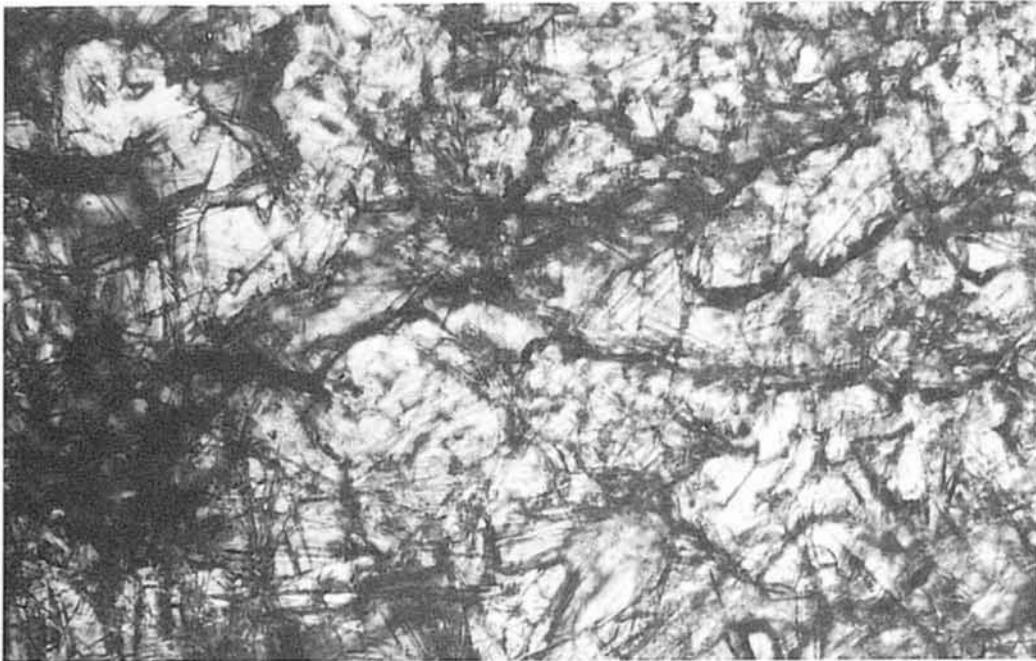


Fig. 6