

Abandoned Smolník mine (Slovakia) – a catchment area affected by mining activities

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Received 28 December 2007

Abstract. Smolník is a historical Cu-mining area that was exploited from the 14th century to 1990. The Smolník mine was definitively closed and flooded in 1990–1994. Acid mine drainage discharging from the flooded mine (pH = 3.83, Fe = 542 mg/l, SO_4^{2-} = 3642 mg/l, Cu = 1880 µg/l, Zn = 9599 µg/l, As = 108 µg/l) acidified and contaminated the Smolník Creek water, which transported pollution into the Hnilec River catchment. The Smolník mine waste area has been used as a model area to document pollution of waters, stream sediments, and soils by metals and other toxic elements. Major goals of this complex study were to document creek water transport of the main pollutants (Fe, sulphates, Cu, Al, As, etc.) in the form of suspended solids, to investigate elements mobility in common mine waste (rock and processing waste heaps and tailing impoundment) and in the soil on the basis of neutralization and leach experiments. Different methodologies and techniques for sampling and chemical and mineralogical characterization of samples were used and checked to evaluate environmental risk of this abandoned mine area.

Key words: mine waste, acid mine drainage, suspended matter, Fe-oxyhydroxides.

INTRODUCTION

Mining industry has created wasteland where large quantities of mine-derived wall rock and tailings have been stocked. Especially mining waste with sulphides has caused large-scale and/or long-term pollution of the environment, because it is able to generate acid mine drainage (AMD). Pyrite easily oxidizes in open-air conditions in mine areas. Moreover, this process is catalyzed by bacteria, which multiply its efficiency to produce acidity (Jambor & Blowes 1994). The most serious consequences include pollution of superficial water and groundwater, contamination of soils, and damage to local ecosystems.

Copper ore (pyrite enriched in Cu) of the Smolník deposit was exploited from the 14th century to 1990. We started to study the Smolník mine area after 1995, when AMD in the so-called first flush strongly damaged the Smolník Creek catchment (e.g. Lintnerová 1996; Lintnerová et al. 1999, 2003, 2006; Šoltés 2007).

The paper presents negative effects of the abandoned sulphide mine on the Smolník Creek catchment. Major objectives of the study were to document the transport of main pollutants by creek water (Fe, sulphates, Cu, Al, As, etc.) in dissolved and suspended solid forms and to investigate the mobility of elements in common types of

mine waste (rock and processing waste heaps, tailings) and in the soil on the basis of neutralization and leach experiments. Different methodologies and techniques for sampling and chemical and mineralogical characterization of samples were used to evaluate environmental risk in this abandoned mine area.

METHODS

Water, precipitates, suspensions, mine waste, and stream sediments were sampled at the monitoring points shown in Fig. 1. (Lintnerová et al. 2003, 2006; Šoltés 2007). Total and partial analyses of stream sediments and alluvial and anthropogenic soils were performed using standardized methods of analyses or the approach published in Sutherland (2002). Especially non-residual parts of soil samples were analysed in 0.5 M HCl leach. The PHREEQC program was used to model equilibrium mineral phases by recalculation of the results of analyses of natural waters and of leaching and precipitation experiments (Parkhurst & Apello 1999). Two sets of samples of AMD and creek water were neutralized by 1 M NaOH and the resulting precipitates and supernatants were analysed (Šoltés 2007). Potential mobility of selected elements in ore and mine waste samples was evaluated

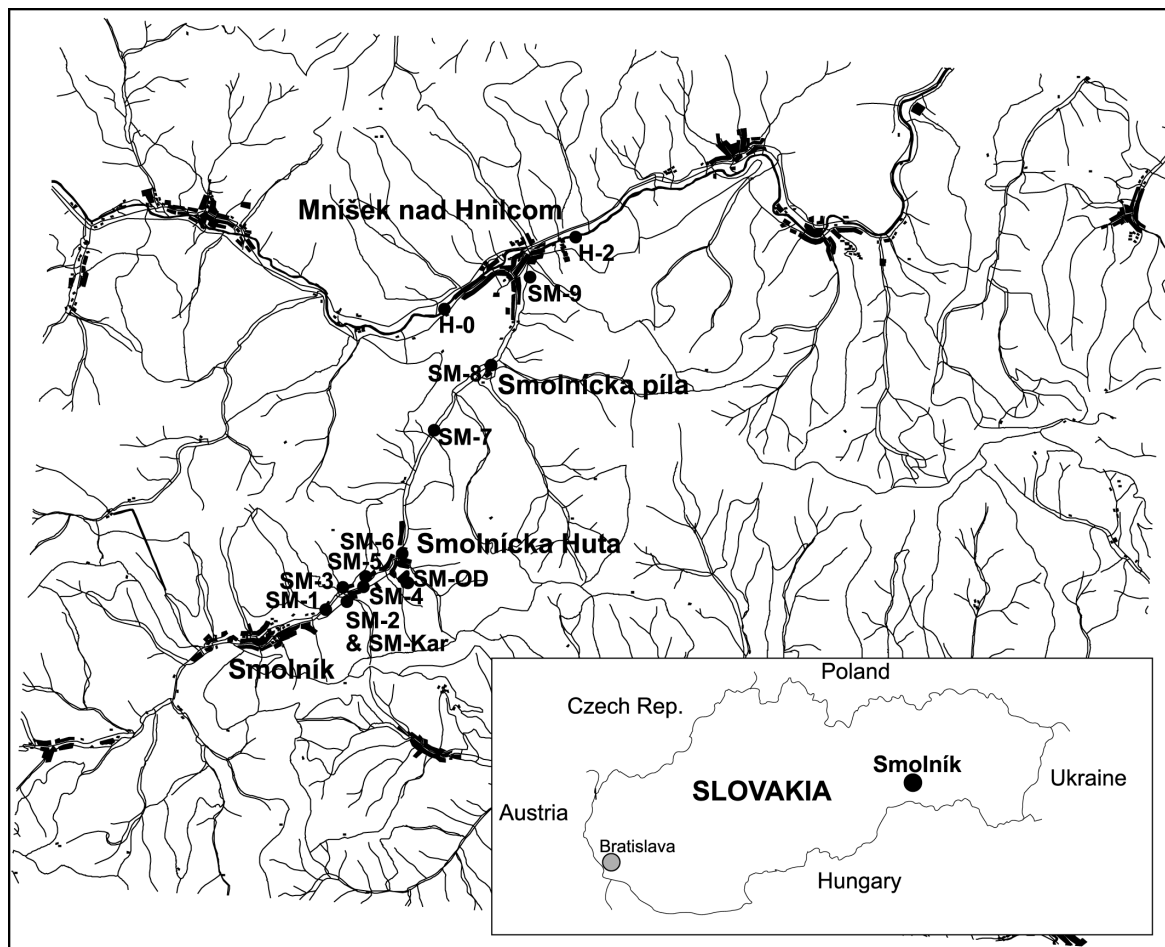


Fig. 1. Location of the Smolník mine (SM-2) and the monitoring points in the Smolník Creek selected in 2002–2003 (after Lintnerová et al. 2006).

from the results of the three sets of batch experiments using the following leach reagents: distilled water, citric acid + sodium citrate, and dilute HNO_3 (Šoltés 2007).

RESULTS

The abandoned Smolník mine is an important and permanent source of contamination in the Smolník Creek with negative impact on the Hnilec River (Table 1). The AMD-outflows (SM-2, SM-Kar.) and seepages (SM-3, SM-5) fall into the hazardous waste category (according to the Council Directive from 12 December 1991, 91/689/EEC). Tailing impoundment in the vicinity of the abandoned mine is the second important source of the creek water contamination, because it permanently produces drainage water with increased contents of Fe, As, and sulphates (SM-OD, Table 1). Various types of

mine water/drainage and waste were studied in the Smolník Creek catchment. The results indicate that each of them contributes a different amount of main contaminants: Fe, sulphates (S_{tot}), Cu, Al, As, Zn, and Mn (Tables 1, 2). Other elements (e.g. Pb, Sn, Se, Cr, Co, Ni, Cd) are potentially or quantitatively less important contaminants. The monitoring of the creek water indicates that the amounts of released pollutants vary seasonally (Lintnerová et al. 2006; Šoltés 2007). The major part of the dissolved mine-derived pollutants precipitate as Fe-oxyhydroxide and sulphate minerals when AMD mixes with creek water (Table 2). The precipitates accumulate under sites of the AMD discharge, in the tailing drainage conduits, and finally in the creek sediments. However, fresh precipitates are extremely fine-grained and are easily removed by the stream in the form of suspended matter (Table 3). Both forms of pollutants, water-dissolved and suspended, play an important role in the mine-derived

Table 1. Average, minimum, and maximum values of selected elements and sulphates in waters from the abandoned mine (SM-2), tailings (SM-OD), and other AMD (SM-3, SM-5, SM-Kar.) pollutants of the Smolník Creek, collected in 2002–2003 (Lintnerová et al. 2006). TDS = total dissolved solids, *n* = number of analyses

	SM-2		SM-OD		SM-3	SM-5	SM-Kar.	
	<i>n</i> = 5		<i>n</i> = 5		<i>n</i> = 1	<i>n</i> = 1	<i>n</i> = 1	
Al	mg/l	82.7	(70.2–92.5)	0.2	(0.1–0.3)	474.0	58.6	159.5
Fe (total)	mg/l	542	(434–659)	5	(2–8)	3 229	321	1 091
Fe ²⁺	mg/l	356	(239–551)	2	(1–3)	421	166	222
Mn	mg/l	35.5	(32.6–38.5)	3.4	(1.2–5.7)	25.3	10.1	170.5
Ca	mg/l	190	(125–249)	44	(19–71)	304	160	2 539
Mg	mg/l	328	(246–385)	37	(15–60)	442	101	1 004
SO ₄ ²⁻	mg/l	3 642	(3 125–4 085)	253	(106–405)	14 800	2 220	9 058
Zn	µg/l	9 599	(6 850–12 040)	45	(31–55)	43 000	7 070	24 405
Pb	µg/l	81	(68–99)		<4	156	18	42.5
As	µg/l	108	(29–380)	46	(14–90)	16 800	140	13
Co	µg/l	697	(483–914)	15	(7–26)	1 810	353	1 524
Ni	µg/l	207	(147–247)	24	(20–29)	625	179	771
Cu	µg/l	1 880	(1 470–2 120)	9	(6–15)	108 000	7 130	13 665
Cd	µg/l	9.2	(7.4–11.1)	3.1	(<0.3–700)	101.3	14.5	21.4
TDS	mg/l	5 127	(4 290–5 990)	467	(228–752)	23 740	3 040	12 401
pH		3.83	(3.27–4.12)	6.76	(6.35–7.38)	2.20	2.95	2.92

Table 2. Contents of the analysed elements and sulphates in the mine drainage precipitates (Lintnerová et al. 2006).

	Precipitates from mine waters				Precipitates from the Smolník Creek		
	SM-2	SM-5	SM-Kar.	SM-OD	SM-4	SM-8	SM-9
	mg/kg						
Fe	42 700	44 900	35 210	33 150	35 130	40 900	20 650
Al	10 000	1 203	500	1 116	–	–	–
As	2 523	842	38.46	10 724	59	14.25	119.33
Pb	459	41	–	78	55	50	188
Zn	77	45	76	1 052	164	345	854
Cu	270	302	68	731	217	1 057	2 164
Mg	1 696	616	–	3 398	–	–	–
Ca	27	77	–	21 031	–	–	–
K	272	551	–	1 978	–	–	–
Na	226	157	–	5 237	–	–	–
Mn	103	35	403	606	168	124	1 973
SO ₄ ²⁻	8 450	842	–	10 724	–	–	–
Se	–	0.52	0.06	–	0.22	0.02	–
Cr	–	3.75	–	8	14.24	–	7.8
Co	–	4.8	8.2	49	7.2	9.4	39.6
Sb	–	3.24	0.57	–	7.15	29.1	6.52

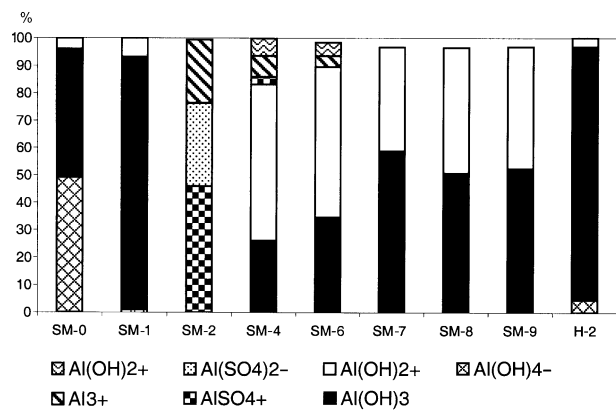
– Not detected.

Table 3. Contents of selected elements in suspended solid samples captured on $>0.45 \mu\text{m}$ membrane from the Smolník Creek water (more details in Lintnerová et al. 2006)

	SM-1	SM-4	SM-6	SM-8	H-0	H-1
Fe %	5.26	12.99	16.34	17.61	8.43	14.60
Al %	1.96	7.96	8.68	6.36	3.71	3.76
As mg/kg	112	142	251	135	124	103
Pb mg/kg	196	171	163	166	150	106
Zn mg/kg	1026	512	798	1235	1079	1979
Cu mg/kg	592	1818	2157	2407	665	1856

contamination, widening in the Smolník Creek catchment, and transport nearly equal volumes of mobilized (mine-derived) elements. On the basis of the measurements conducted in 2002–2003 we estimated that approximately 280 kg of Fe, 3.54 kg of Cu, and 1.44 kg Zn per day in suspended solids could have been transported by creek water into the river (measured near the creek–river confluence in the average runoff and climatic conditions).

Assumed changes in element species in the creek water, caused by the inflow of AMD to the creek, and saturation indices (SI) of mineral phases were calculated using the PHREEQC program (Parkhurst & Apello 1999; Šoltés 2007). For example, the Al species most hazardous to living organisms, AlSO_4^+ and Al^{3+} , predominated in water under the site of AMD inflow (Fig. 2). The distribution of SI values corresponds to the Fe-oxhydroxide

**Fig. 2.** Speciation of Al in water samples from the Smolník Creek (SM) and the Hnilec River (H-2).

mineral phases observed in the natural precipitates when AMD is mixed with the creek water. The results of the modelling of water composition indicate that small changes in pH and water temperature could explain the observed seasonal changes in mineral composition (indicated also by changes in colour) and/or mineral distribution in the area during different seasons.

Generation of solid matter/precipitates was studied experimentally in the laboratory, using the analysed samples of AMD and creek water. The results documented progressive precipitation of amorphous Fe-oxhydroxide and co-precipitation or capture of Al, Cu, Zn, and Mn into the solids with increasing pH (Table 4).

Table 4. Content of elements after progressive neutralization of samples from K-0 to K-5 (Karitas) and SM-2/0 (New drainage) by 1 M NaOH in supernatants expressed in wt % of the initial content of the element. * measured 65 hours after neutralization

Sample	pH	Eh	Fe	Al	Zn	Cu	Mn	SO_4^{2-}
	65 hours*	mV						
K-0	2.52	611	0	0	0	0	0	0
K-1	2.74	460	19.48	91.69	0	74.85	0	4.31
K-2	3.43	346	59.85	99.51	40.86	94.65	0	4.14
K-3	4.14	220	90.96	99.84	89.9	99.25	1.51	4.28
K-4	6.33	–6	99.91	99.59	98.82	99.25	20.64	3.91
K-5	7.98	–104	99.96	99.59	99.72	99.44	20.75	5.39
SM-2/0	2.73	454	0	0	0	0	0	0
SM-2/1	4.45	190	63.93	3.49	0	2.04	0	1.89
SM-2/2	5.33	64	50.24	25.42	0.34	12.64	0.79	1.71
SM-2/3	6.36	–63	50.86	93.42	16.61	50.79	0.46	9.24
SM-2/4	7.54	–67	75.97	99.92	78.56	99.34	6.15	15.09
SM-2/5	8.3	–7	99.97	99.83	99.69	99.94	67.14	10.41

Initial content of element in water, mg/l

K-0	2.52	611	301.6	83.6	9.1	1.59	27.8	2839
SM-2/0	2.73	454	536	155	19.3	13.1	126.4	7275

Contents of sulphates are low in all solids probably due to the high content of Na⁺, which hampered precipitation of the assumed mineral phases with high positive SI, e.g. schwertmannite (Rosse & Elliot 2000; Jönsson et al. 2005). Less typical phases (e.g. hexahydrate or Na-Fe sulphates and gypsum) were identified in dried products (Šoltés 2007). Products were transformed progressively to goethite (Fig. 3). Relatively crystalline goethite was identified by X-ray analyses of products after elimination of dissolved salts by dialysis in distilled water. Feryhydrite and goethite occurred in precipitates when AMD samples were neutralized/diluted by water from the creek (SM-1) with diminutive NaOH adds and after 65 days “ripening” in stabilized pH and normal temperature conditions.

The aim of the experimental leach was to document the mobility of elements in rocks with pyrite, ores and in metallurgic slag samples and to estimate pollution potentials of these common materials in the mine waste area. The experimental study confirmed high Fe, Cu, and Zn leaching ability under strong acid conditions. The leaching kinetics of elements depend on the initial content of elements, their presence in more soluble forms/minerals, and many other properties (e.g. grain size, surface activity, secondary mineral coats). Weathered waste (e.g. recent to “ancient” heaps) continually supplied

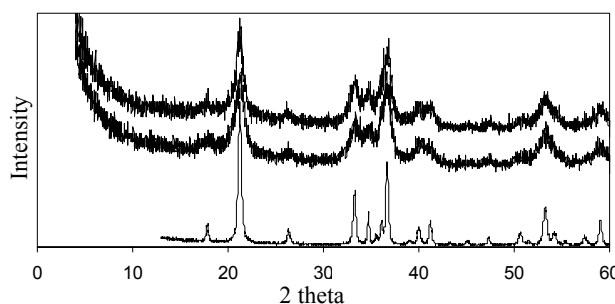


Fig. 3. X-ray records of the neutralization product (from top to bottom): SM-2/1, K-1, ideal record of goethite.

sulphates, iron, Cu, and other elements to pore water and therefore they could accumulate in soils.

Alluvial soils of the Smolník Creek catchment and anthropogenic soils covering mine waste were also studied. The simple 0.5 M HCl leach approach was used to estimate the non-residual content of elements (Sutherland 2002), because pH monitoring documented extreme soil acidity (pH <3 to 4) in the mine-waste area. The total content of Fe, Mn, Cu, Zn, and As demonstrates the geochemically anomalous character of these near-deposit soils when compared to the national limit of risky elements in soils (Table 5). The increased contents of non-residual Cu, Zn, and Mn were observed in strong-

Table 5. Total (analysed after total dissolution) and non-residual (analysed in 0.5 M HCl leach) contents of elements in soil samples collected in 2002. SM-1 = sample point, 5–15 = depth in cm, DRP – samples from the abandoned mine area near the monitoring point SM-2, not presented in the map in Fig. 1

Sample	Fe, %		Mn, mg/kg		Cu, mg/kg		Zn, mg/kg		As, mg/kg	
	Total	HCl	Total	HCl	Total	HCl	Total	HCl	Total	HCl
Alluvial soil										
SM-1/5–15	5.06	1.21	1190	580	234	170	194	106	64	1.66
SM-4/5–15	7.96	1.68	590	248	376	183	187	53	315	10.4
SM-6/5–15	8.13	1.36	850	316	436	191	235	113	304	0.82
SM-7/5–15	6.57	2.24	440	358	448	213	170	147	180	1.58
SM-8/5–15	8.27	3.54	740	293	698	443	202	97	107	2.03
SM-7L/5–15	6.16	2.01	1550	1025	1435	875	372	199	92	3.71
SM-7L/20–30	5.19	1.06	1390	84	961	650	233	104	49	1.17
SM-7N/5–15	5.67	1.4	930	510	310	175	213	115	82	2.13
SM-7N/15–25	9.83	4.82	830	401	605	290	330	167	136	2.06
SM-7N/30–40	8.57	3.45	1070	590	537	171	288	155	122	1.76
SM-7N/40–50	8.69	3.22	1100	550	609	223	280	145	127	2.18
SM-7N/50–60	7.27	2.29	630	188	686	358	305	150	125	2.39
Court – constructed soil cover										
DRP-4/20–30	12.66	2.92	730	54	1558	167	315	28	1310	6.19
DRP-5/0–15	10.19	2.38	460	68	261	56	105	19	772	1.26
DRP-5/15–25	8.98	2.34	40	64	222	63	89	18	406	0.95

to medium-acid alluvial soil samples. It is important that As is not intensively liberated from residual (lithogenic) components of alluvial soil (Table 5). However, high non-residual contents of As, Al, and Cu were detected in samples of anthropogenic soils from old dumps and also from the recently “constructed” soil cover in the previous mine-work area (Tables 5 and 6, court). High As content is obviously combined with fresh amorphous Fe-oxyhydroxides precipitated near the sites where acid drainages discharge to the air, i.e. mainly near the abandoned mine and tailing impoundment (Tables 2, 3).

A previous multistep sequential study documented that the largest part of metals in the Smolník Creek sediment is bounded to or adsorbed by Fe-oxides and by organic matter (Lintnerová et al. 2003). The contents of exchangeable or bioavailable Fe, Cu, Zn, and Mn have increased due to the generation of AMD and its high-leach potential. In the polluted parts of the creek the amount of Fe-oxyhydroxide phases accompanied by other mine-derived elements is comparable to the amount of elements bounded in the residual part of the sediments. Bioavailability of elements could potentially increase due to transformation of “fresh” Fe-oxyhydroxides into stream sediments.

The results of soil analyses indicate that simple leaching by dilute (0.5 M) HCl could be a valuable tool in environmental assessment. These results are less selective than multistep sequential analyses but highly informative, while the analytical approach is rapid and cost-effective.

CONCLUSIONS

A flooded mine is a permanent source of acid mine water with stabilized (or balanced) composition. The environmental risk of the area will have the tendency to lowering its “hazardous content”. Human activity in the mine-waste area is a very important risk factor, which includes especially the mining waste management, the utilization of the area, and the remediation and construction of an AMD treatment plant eventually. Negative impacts (exploitation of dumps, mine and dump stability changes, covering by landslide, and changes in ground water circulation) on this relatively stabilized environment will probably accelerate mobilization of potentially toxic elements and decrease pH of mine water. Otherwise, stabilization of mine dumps, maintenance of superficial water drainage in the waste area, and final

Table 6. Non-residual contents of elements in soil samples collected in 2006. All samples from the 5–15 cm depth, K-1, CK-1/2, C-1/2, B-1/2, Rotenberg – samples from mine dumps, pyrite K-2/3, pyrite K-2/4 – recultivated area in the vicinity of the monitoring point SM-2, not presented in the map in Fig. 1

Sample	Fe	Al	Mn	Zn	Cu	As
	%	mg/kg				
Alluvial soil – bank of the Smolník Creek						
SM-1	3.76	11 950	840	157	429	35
SM-Kar	8.33	10 800	484	120	580	354
SM-7 1/2	4.67	12 450	695	252	810	93
SM-7 2/2	2.40	10 250	525	81	262	24
SM-7 5/6	4.88	9 200	540	127	378	82
Heaps – anthropogenic soils						
Depression	2.08	20 600	130	177	6 410	63
K-1/3	7.64	14 500	337	84	1 960	170
CK-1/2	5.59	8 200	1 165	42	310	33
C-1/2	8.81	17 700	333	197	630	735
B-1/2	6.71	11 700	232	61	385	27
Rotenberg	12.14	12 200	217	92	680	487
Court – constructed soil cover						
Pyrite K-2/3	6.23	6 200	145	49	2 975	640
Pyrite K-2/4	3.16	10 000	270	79	55	4 027

remediation would prevent increase in contamination and speed up the return to the initial or natural geochemical level of contamination, which is limited by the geological environment.

ACKNOWLEDGEMENTS

This work was supported by the Slovak VEGA fund (project No. 1/3072/06) and the Slovak Research and Development Agency under the contract APVV-0268-06 “Contamination generated by Sb mining in Slovakia; Evaluation and strategies for remediation”.

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Kaevandamisest mõjustatud valgala – maha jäetud kaevandus Smolníkis (Slovakkias)

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Smolník on ajalooline vasekaevandamisala, mida eksploateeriti alates 14. sajandist kuni 1990. aastani. Smolníki kaevandus suleti ja uputati aastail 1990–1994. Happelised kaevanduse heitveed ($\text{pH} = 3,83$, $\text{Fe} = 542 \text{ mg/l}$, $\text{SO}_4^{2-} = 3642 \text{ mg/l}$, $\text{Cu} = 1880 \text{ } \mu\text{g/l}$, $\text{Zn} = 9599 \text{ } \mu\text{g/l}$, $\text{As} = 108 \text{ } \mu\text{g/l}$) hapestasid ja saastasid Smolníki oja vee, mis kandis reostuse Hnileci jõe valgale. Smolníki kaevanduse aheraine ladustusala on kasutatud mudelalana, dokumenteerimaks vee, oja sāngi setete ja pinnase (mulla) saastatust metallide ning teiste toksiliste elementidega. Kompleksuuringu peamisi eesmäärke on olnud jälgida olulisemate saasteainete (Fe, sulfaadid, Cu, Al, As jt) edasikannet suspensioonidena oja vees, uurimaks elementide mobiilsust tavalistes aheraine puistangutes (rikastamis- ja töötlemisjääkides ning liivahoidlates), aga ka pinnastes, eriti muldades nii neutraliseerimis- kui ka leostamiskatsete alusel. Eri keemilisi ja mine-raloogilisi meetodeid kasutades on hinnatud maha jäetud kaevanduse keskkonnaohtlikkuse määra.