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**LEACHABILITY AND THERMAL STABILITY OF SYNTHESISED
AND NATURAL SVABITE**

**ŁUGOWALNOŚĆ I STABILNOŚĆ TERMICZNA
SWABITU SYNTETYCZNEGO I NATURALNEGO**

Currently, arsenic is removed from blister copper by soda and calcium hydroxide injection into liquid metal. In consequence sodium and calcium arsenates are formed. These arsenates could be converted to analogues of minerals, which naturally contain high concentration of arsenic and are known to be durable over geological time and slightly soluble in water. The project attempted to show that sodium arsenate contained in slag could be converted into svabite $\text{Ca}_3(\text{AsO}_4)_3\text{F}$ which is being considered for safe disposal of arsenic. The thermal stability of the synthesised svabite under low oxygen pressure was also determined.

Arsen usuwa się z miedzi w wyniku wdmuchiwania do ciekłego metalu sody (Na_2CO_3) oraz wodorotlenku wapnia ($\text{Ca}(\text{OH})_2$) celem utworzenia stabilnych arsenianów sodu i wapnia. Z otrzymanych arsenianów możemy utworzyć związki odpowiadające składem minerałom występującym w przyrodzie. Związki te charakteryzują się trwałością w wymiarze geologicznym i małą rozpuszczalnością w wodzie. Celem badań było pokazanie możliwości przeprowadzenia arsenianu sodowego (Na_3AsO_4), który znajduje się w żużlach rafinacyjnych miedzi w swabit $\text{Ca}_3(\text{AsO}_4)_3\text{F}$. Minerale ten występuje w przyrodzie, wykazuje minimalną rozpuszczalność w wodzie i dlatego nadaje się do bezpiecznego składowania arsenu. Ponadto, zbadano stabilność otrzymanego związku w podwyższonych temperaturach i pod obniżonym ciśnieniem tlenu.

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1. Introduction

The copper industry in Poland has to remove arsenic from blister copper, as its concentration constantly increases because of increasing arsenic content in smelting concentrates. Arsenic is removed by soda and calcium hydroxide injected into blister. In consequence sodium and calcium arsenates are formed. Arsenic slags containing these arsenates are reverted into the process, therefore arsenic content in materials stream has considerably increased. The future of arsenic bearing compounds remains open question, because of limited consumption and decreasing market demand. A possible solution to the problem is to synthesise analogues of minerals, which naturally contain high concentration of the arsenic and are known to be durable over geological time and slightly soluble in water. Such method is called Synthetic Mineral Immobilisation Technology (SMITE) [1–4]. This approach gained public acceptance, because the idea is well understood by laypersons. Currently used immobilisation method of arsenic is based on the formation of iron arsenates [5–6]. The solubility of amorphous scorodite $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ is high and exceeds official environmental protection limits. However, it has been shown [6] that for crystalline scorodite and ferric arsenates with Fe/As ratio greater than 4, arsenic solubility is quite low, and therefore these compounds could be used for arsenic stabilisation. Nevertheless, ferric arsenates may not meet future regulations, and therefore we should seek much more reliable method for arsenic stabilisation.

This project attempts to utilise SMITE technology for immobilisation of sodium arsenate contained in slag formed during arsenic removal from blister by converting it into svabite $\text{Ca}_5(\text{AsO}_4)_3\text{F}$.

The presented part of this project is devoted to investigation of leachability of synthesised svabite from pure components as well as a natural mineral. Arsenic solubility in water during leaching of these minerals was investigated as a function of pH. The arsenic solubility decreases when pH of the solution increases. The slurry was buffered at about 9.4 pH, regardless of the acidity of the original solution, if its initial pH was higher than 4.

2. Methods and materials

The aim of these investigations was to collect solubility data for both synthesised and natural svabite. Two procedures were employed to synthesise the svabite, and in both cases all chemicals used in this work were reagent grade.

Procedure 1

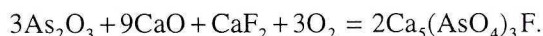
10 g of As_2O_3 , 8.503 g of CaO and 1.315 g of CaF_2 was placed in 250 ml polypropylene bottle and mixed with 30 ml of distilled water. Then 1 ml of 10% solution of sodium hydroxide (to catalyse the reaction) and 20 ml of distilled water

was added to form creamy slurry. The bottle was stoppered and left for 18 hours. After the equilibration, the slurry were filtered with Buchner apparatus and Whatman paper. Precipitate was shaped in the form of three spheres and oven dried at 100°C for 16 hours. Next the samples were sintered in two temperatures at 500°C for 18 hrs and then at 1300°C also for 18 hrs. This was done in order to convert arsenic to the pentavalent state and promote crystallisation of svabite.

Procedure II

10 g of As₂O₃, 8.503 g of CaO and 1.315 g of CaF₂ was placed in 250 ml polypropylene flask and mixed with 30 ml of distilled water. Then 50 ml of 30% solution H₂O₂ was added very slowly because of the very vigorous reaction and temperature increase of the sample. The flask was stoppered and left for 18 hrs. Next operations were identical as in procedure I.

The overall reaction in both cases was:



X-ray diffraction confirmed that svabite was the dominant product, and chemical analysis of the sample gave 35.4 wt% As content in the tested material.

Durability of the obtained product was investigated by leaching it with water of different pH and temperatures.

3. Results

Three different methods were used to obtain solubility data for Ca₅(AsO₄)₃F. In these experiments, leachants were prepared with pH values of 1–9 utilising 0.25M H₂SO₄ and 0.1M NaOH. The first method was to investigate the svabite behaviour at water boiling temperature. The sintered svabite sphere was put into a one side closed long glass tube (700 mm length, 28 mm outer diameter) with 50 ml distilled water. The tube was stoppered and put into the oil bath heated to 108°C. The constantly boiling water generated vapour, which was condensed on the cold part of the glass tube, and therefore the same water leached the sample. After the equilibration time (24, 72 or 148 hrs), the solution was sampled, filtered and analysed for arsenic content. The remaining solution was replaced with fresh distilled water of the same volume and pH. The results are listed in Table 1. Boiling water leach tests confirmed high durability of the svabite in crystalline form.

The second method was designated to simulate the behaviour of svabite in dumping areas, where the mineral would be leached by fresh water. The experiments were performed at ambient temperature for periods 6,7,8,14 and 15 days. The svabite samples were grounded (<0.2 mm) and slurred in distilled water of predetermined pH at 10 g

TABLE 1

Effect of leaching time on arsenic content in distilled water (pH = 6.5) at 100°C

Leaching time, hrs	Concentration of As in the water, mg • l ⁻¹		pH of the water after leaching	
	Svabite-procedure I	Svabite-procedure II	Svabite-procedure I	Svabite-procedure II
24	0.15	0.14	9.46	7.52
72	0.12	0.18	8.72	7.22
148	0.27	0.19	8.13	7.18

solids per litre. The samples were agitated twice per day. In the experimental time pH was checked several times, and readjusted if required. After the equilibration time, the slurry was settled and the solution was sampled, filtered and analysed for arsenic content. The remaining solution was decanted and replaced with fresh distilled water of the same volume and pH. The procedure was repeated until constant arsenic content in the solution was obtained. The results of these tests are listed in Table 2 and summarised in Figure 1. As it was expected, in the first periods losses were relatively high.

TABLE 2

Results of svabite leaching according to the second method (pH constant).
Leaching temperature 20.7±1.2°C

Test number	pH of the solution	Time of leaching, hrs	As in solution, mg • l ⁻¹
1	5.02	144	564
	6.01		200
	6.98		41.9
2	5.02	168	479
	6.01		89.2
	7.04		34.0
3	5.02	192	357
	6.01		113.7
	6.98		33.6
4	5.02	336	249.0
	6.01		247.0
	6.98		37.9
5	5.02	360	190
	6.01		211
	6.98		38.8

The third method was carried out in order to obtain solubility data for long term leaching. The samples were grounded (<0.2mm), slurred in distilled water of predominated pH at 10 g solids per litre and equilibrated for 14 days. The samples were agitated twice per day. After this time solution samples were withdrawn, filtered and subjected to analyses for arsenic content. The pH of the solutions was also determined.

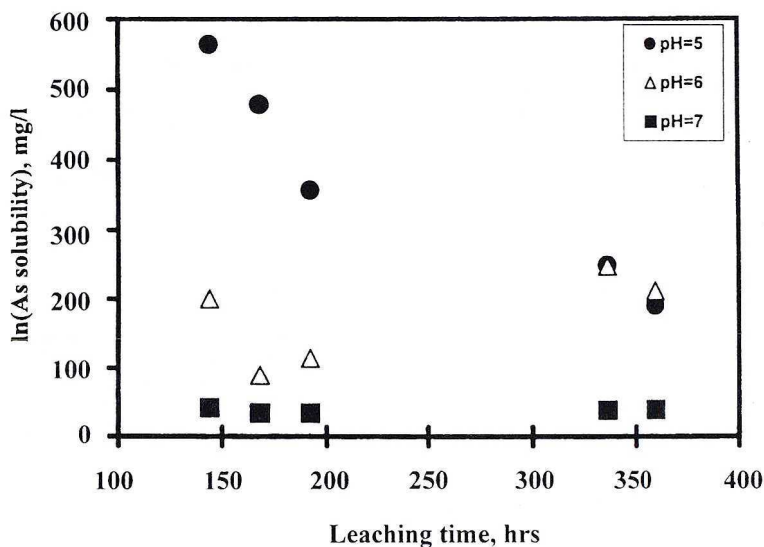


Fig. 1. Arsenic solubility as a function of leaching (according to second method) time at $20.7 \pm 1.2^\circ\text{C}$

To compare durability of the synthesised and natural svabites, the same leaching tests were carried out with a natural mineral. Results are listed in Table 3 and illustrated in Figure 2. The rapid fall off in intrinsic leachability of the synthesised as well as natural svabite is observed for leachants with pH varied between 1 and 5.

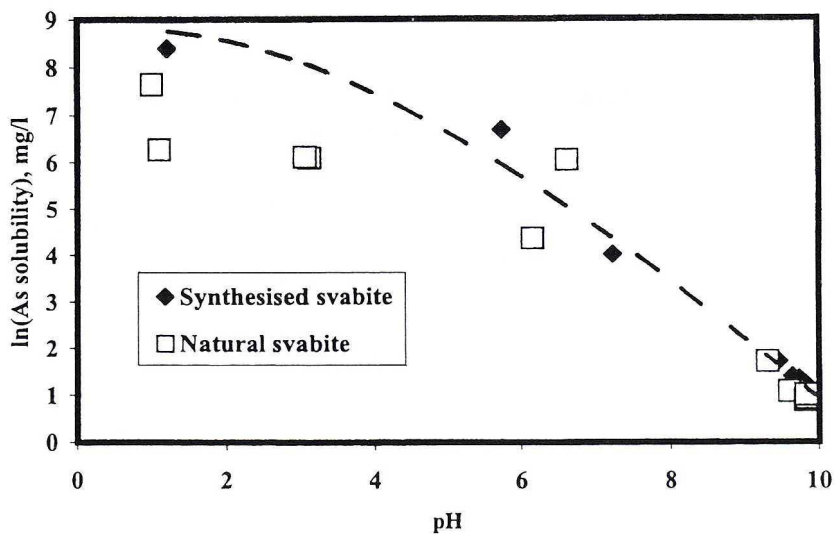


Fig. 2. Solubilities of natural and synthesised svabites at $20 \pm 2^\circ\text{C}$

TABLE 3
The solubility of arsenic as a function of pH of leaching solution at $20 \pm 2^\circ\text{C}$

Sample	pH at beginning	pH after test	As in solution, $\text{mg} \cdot \text{l}^{-1}$
Synthesised svabite	1.08	1.21	4410
	2.02	5.74	800
	2.99	7.22	54
	4.01	9.47	5.5
	5.02	9.65	4.0
	5.46	9.74	3.8
	6.00	9.73	3.5
	6.47	9.78	3.6
	6.98	9.75	3.5
	7.59	9.80	3.4
	7.96	9.82	3.45
	8.98	9.83	3.20
Natural svabite	0.97	1.00	2080
	0.99	1.10	530
	1.97	3.11	440
	2.01	3.05	450
	3.01	6.61	420
	3.01	6.15	77
	3.99	9.32	5.5
	5.01	9.66	2.9
	6.01	9.61	2.9
	6.98	9.85	2.4
	7.99	9.82	2.4
	8.99	9.83	2.5
		8.99	9.83

4. Svabite stability investigation at high temperature and low oxygen pressure

Two measures can be taken to provide an added barrier to remobilization of the svabite. The svabite can be encapsulated with a minimum of Portland cement or dissolved in discarded slag. The second option seems to be suitable in this case, however stability of svabite at elevated temperature and low oxygen pressure should be well established.

The stability tests for synthesised svabite were carried out at elevated temperatures (1373, 1423 and 1473 K) and under low oxygen pressures ($P_{\text{O}_2} = 10^{-8}, 10^{-9}, 10^{-10}$ atm). The samples of 10 g were kept at hot zone of the vertical furnace, and the oxygen pressure was maintained by CO-CO₂ mixture passing throughout the reaction tube of the furnace for 24 hours. After cooling, the samples were removed from the furnace and weighted. Next, the samples were chemically analysed for As content and by X-ray diffraction technique. The results are listed in Table 4, and summarised in Figure 3.

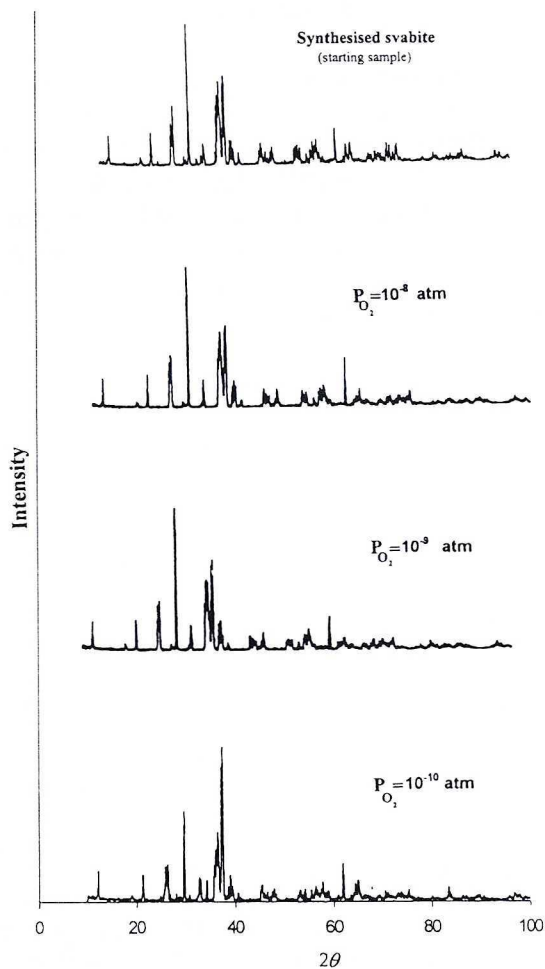


Fig. 3. X-ray diffraction pattern of svabites heated at 1200°C for 24 hrs and under different oxygen pressures

TABLE 4

Arsenic content in svabite and mass losses after stability tests

Oxygen pressure, atm	T = 1373 K		T = 1423 K		T = 1473 K	
	Mass losses, %	As content, wt%	Mass losses, %	As content, wt%	Mass losses, %	As content, wt%
10^{-8}	—	—	—	—	0.72	34.4
10^{-9}	—	—	—	—	2.61	33.7
10^{-10}	0.83	35.5	3.33	33.1	25.21	33.8

Theoretical content of arsenic in svabite is 35.33%

5. Summary

These results demonstrate usefulness of svabite for arsenic immobilisation. It is very important that svabite increases pH of leaching groundwaters, which in turn decreases the arsenic solubility. The high arsenic loading achieved in the svabite can extend the lifetime of a depository landfill. Thermal stability of the svabite decreases very rapidly at temperatures above 1373K and under low oxygen pressure ($P_{O_2} < 10^{-9}$ atm). Generally, the sintered svabite proved far more resistant to leaching than powdered material. This phenomenon may suggest easy removal of arsenic from a damaged surface layer.

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