

RECOVERY OF GERMANIUM BY PRECIPITATION FROM STRONGLY ALKALINE SOLUTION

M.Sc. Andrzej Piotrowicz¹

Assoc. Prof. Dr. Sc. Stanisław Pietrzyk²

Artur Puchala³

^{1, 2, 3} AGH University of Science and Technology, Poland

ABSTRACT

The research material was a strongly alkaline solution containing germanium, lead, arsenic, zinc and trace amounts of other metals, obtained by leaching of industrial material. This study aimed to determine the behavior of the above metals in the precipitation process using various acidic agents: HCl, H₂SO₄, C₂H₂O₄, C₆H₈O₇. The tests were carried out in a wide pH range. The behavior and role of individual ions during the acidification of germanate solution is poorly understood, hence the study of this subject was undertaken.

The resulting precipitates and solutions were examined by *XRF*, *XRD* and *ICP* techniques. The recovery yields of individual elements was determined. Attempts were also made to precipitate Ge from a synthetic solution in order to compare the results obtained for the solution of an industrial solution.

This research shows that the presence of other ions interferes with the selective recovery of Ge from research solutions. Generally, it can be said that the method of recovery by acidification is effective at low concentrations of the solution's components.

Keywords: *germanium recovery, heavy metals metallurgy, hydrometallurgy*

INTRODUCTION

Recovery of germanium (Ge) from solution depends on the chemical form in which germanium is. Most often, Ge is recovered by acid leaching and precipitation [1], [2], [3], [4], solvent extraction [5], [6] or by the distillation of GeCl₄ [7], [8], [9]. Much less often, recovery occurs from alkaline solutions [1], [7], [10], [11] and due to the fact that more valuable reagents (concentrated caustic soda) are required and technological conditions are more difficult (high temperature process, high viscosity of solution etc.).

Precipitation of Ge from alkaline solutions can be carried out by acidification, according to E_H-pH diagram of Ge-Na-H₂O system [12]. Another method of Ge recovery is using of magnesium salts to form germanates [1], [10], [13], [14]. In recycling processes, almost always Ge is accompanied by other elements, especially silicon, arsenic, heavy and rare metals. The presence of other elements may turn out to be crucial. Arsenic is such an element that should be avoided due to co-distillation with GeCl₄ during refining by distillation. Silicon and lead are chemically similar to Ge and also undergo alkaline leaching, which explain their co-occurrence.

OBJECTIVES

The objective of this study was to investigate the recovery of germanium, in accompaniment of other elements, from an alkaline solution by changing pH (acidification). The chemical composition of the experiment's products was examined. The recovery yields were determined. It was verified whether the above tests are comparable to recovery from a synthetic solution.

EXPERIMENTAL AND MATERIALS

The research material was an industrial strongly alkaline (pH approx. 14) sodium hydroxide solution containing Ge, Pb, As, Zn and others elements. The recovery proceeded using either acids: sulfuric (H₂SO₄), hydrochloric (HCl), citric (C₆H₈O₇) and oxalic (C₂H₂O₄). The precipitation was carried out in the following order:

1. 40 ml of the solution was stirred at 200 rpm and the acid was added via a dropping funnel until the given pH was reached;
2. after 15 min the pH value was read;
3. gravity filtration was performed, the precipitate was rinsed and then dried in air for 24 h.

Recovery tests was carried out in 250 ml beakers (*BOMEX* glasses). Quantitative medium filters (*EUROCHEM*, Poland) were used for filtration. Reaction products were rinsed with distilled water or 80% ethanol (in the case of precipitates obtained using C₂H₂O₄, to prevent the chromatography effect) using approx. 200 ml rinsing medium.

Experiments were carried out on a magnetic stirrer with a heating plate – *LGG-uniSTIRRER7*. The parameter characterizing precipitation with acids is pH of the solution. pH values were recorded with an *ELMTRON CX-741* multimeter. The pehameter (pH-electrode type *ERH-13-6*, *Hydromet*, Poland) was calibrated with buffers (*Hamilton Duracal*). Each solid product was analyzed quantitative by energy disperse X-ray fluorescence technique (*ED-XRF*, *MiniPal4 PANalytical*), and qualitative by X-ray powder diffraction analysis (*XRD*, *Rigaku MiniFlex II*). Also additional analyses were performed: inductively coupled plasma – mass spectroscopy (*ICP-MS*, *ELAN 6100 Perkin Elmer*) and thermogravimetry (*TGA*, *SDT Q600 TA Instruments*) – for C₂H₂O₄ and C₆H₈O₇. Results from these analyses allowed the characterization of products and calculation of the recovery yields (η_X):

$$\eta_X = \frac{(m_\tau - m_R) \cdot \frac{c_{X,\tau}}{100}}{V_0 \cdot c_{X,0}} \cdot 100\% \quad (1)$$

where: V_0 – initial volume of solution [ml]; $c_{X,0}$ - initial concentration of X in solution [g·ml⁻¹]; m_τ – solid product mass [g]; m_R – mass of acid moiety in solid product [g]; $c_{X,\tau}$ – concentration of X in solid product [wt.%]; concentrations of X in solutions were determined by *ICP-MS* and in solid products by *EDXRF*; X is Na, S, Cl, Fe, Ni, Cu, Zn, Ga, Ge, As, Ag, In, Sn or Pb; mass of acid moiety were determined by *TGA* (applies of cases of precipitation with using organic acids).

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For the preparation of acids solutions were used 95% H₂SO₄, 35÷39% HCl, C₆H₈O₇·H₂O (p.a., *Avantor*, Poland) and distilled water ($\kappa=0,07\pm0,01 \mu\text{S}\cdot\text{cm}^{-1}$); oxalic acid (p.a. C₂H₂O₄·2H₂O, *Avantor*) was in the form of alcoholic solution (the solvent was an 80% ethanol which prepared from 99.8% C₂H₅O₅, p.a., *Chempur*, Poland).

Tests on synthetic solution (*SS*) proceeded similarly to experiments on an industrial solution (*IS*) with using acids. The *SS* was obtained by alkaline leaching with a sodium hydroxide solution of the synthetic mixture. This mixture consisted of the following compounds: calcined Scheele's Green (50.20 wt.% CuO, 44.9 wt.% As₂O₃, at 400°C for 1 h), In₂O₃ obtained from metallic In by oxidation in air (950°C, 10 h), Fe₂O₃, CuO, ZnO, GeO₂, Ag, SnO, PbO (all of the above were p.a., *Avantor*) in such proportions that the final composition of the *SS* is approximate to the *IS*.

RESULTS AND DISCUSSION

Comparing the chemical compositions of *IS* and *SS* (Tab. 1), it can be seen that Na, Sn and Pb contents are comparable in both solutions, while the other components are not. In *SS*, there is more Ni, Cu and Zn, but less Ge and As. It follows that the composition of the synthetic mixture does not correspond the composition of the industrial material, in which these components are not just in the oxides form, but in other, difficult leachable in alkali. In₂O₃ and Ag do not leach out.

Table 1. Compositions of IS and SS, ICP-MS analysis, components calculated as oxides

	Na ₂ O	NiO	CuO	ZnO	Ga ₂ O ₃	GeO ₂	As ₂ O ₃	SnO	PbO	other
	wt.%									
<i>IS</i>	28.7	0.081	0.257	1.037	0.009	3.47	3.77	0.24	58.3	4.14
<i>SS</i>	26.2	3.375	1.074	6.472	0.000	2.01	1.31	0.34	56.1	3.12

Depending of the chemical agent used for recovery studies, the phase composition of the resulting solid was different. In case of using H₂SO₄ (Fig. 1), co-precipitation of Pb₅(GeO₄)₂(SO₄) and NaPb(AsO₄)₃ takes place in the pH range 10.71-7.20, and also additionally Na₂GeO₃ at pH 9.39 and 7.20. Na₂GeO₃ phase disappears at a pH below 7.20. Precipitates obtained at pH 5.69 and 4.79 consist Pb₅(GeO₄)₂(SO₄) and PbSO₄, while below pH 4.79 practically only PbSO₄. Precipitation with using HCl (Fig. 2) causes the appearance of Pb₅(AsO₄)₃Cl phase in the whole pH range. In addition, the Pb₅Ge₃O₁₁ phase is present at pH range 10.91-7.22. PbCl₂ phase is recorded for pH 5.91 and 4.93 (several reflexes in the range of 2θ from 23 to 41 deg). Using C₆H₈O₇ (Fig. 3) is obtained precipitates composed of the following phases: Pb₅Ge₃O₁₁, NaPb₄(AsO₄)₃ and Pb₅(AsO₄)₃OH. Below pH 5.73 no precipitates are received. The use of C₂H₂O₄ (Fig. 4) causes the precipitation of oxalate salts: C₂Na₂O₄ (alkali neutralization) in the whole pH range, as well as C₂PbO₄ (form plumbates) below pH 7.56. For pH=2.07, C₂Na₂O₄ phase disappears and C₂HNaO₄·H₂O phase appears.

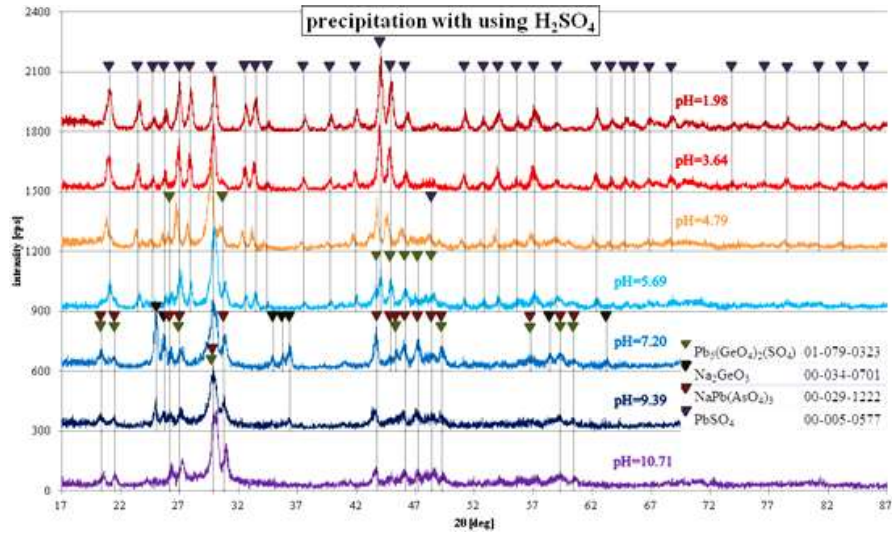


Fig. 1. XRD patterns of precipitates obtained by using H₂SO₄ at different pH

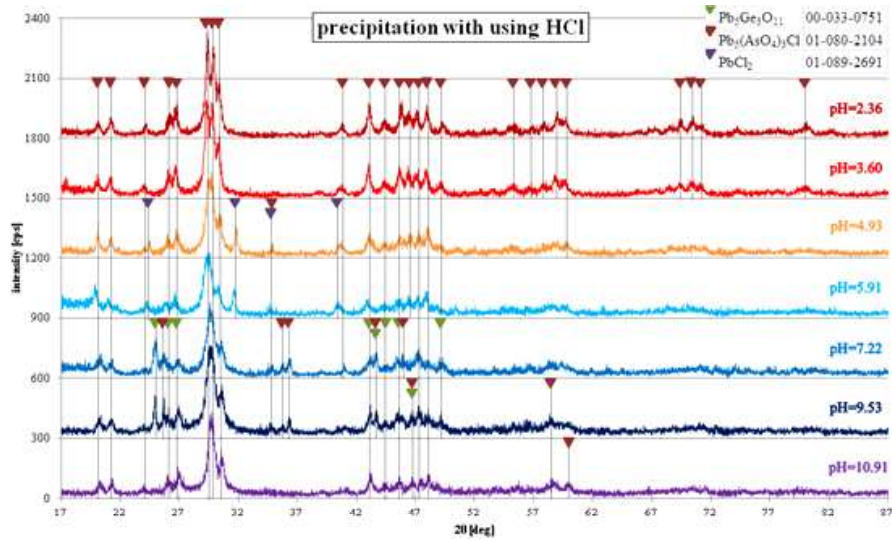


Fig. 2. XRD patterns of precipitates obtained by using HCl at different pH

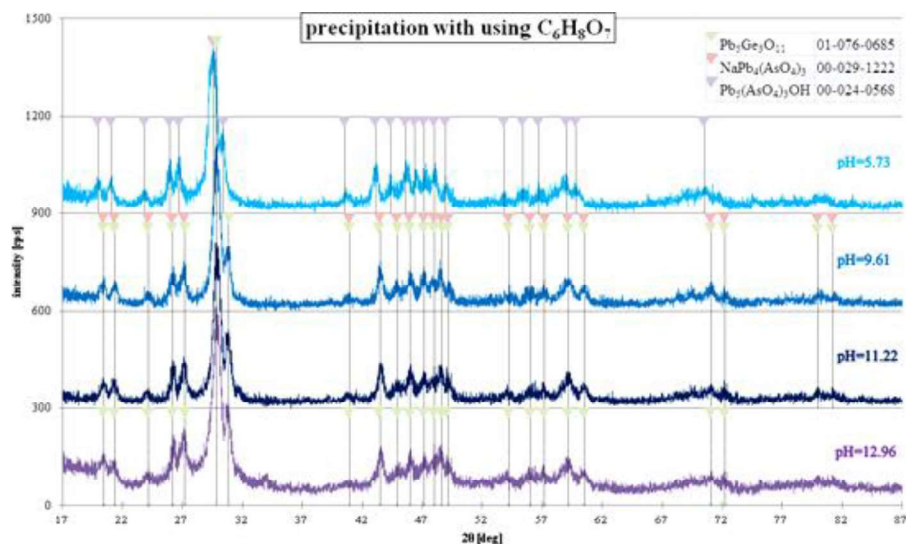


Fig. 3. XRD patterns of precipitates obtained by using $C_6H_8O_7$ at different pH

Fig. 5-8 show recovery yield results for H_2SO_4 , HCl , $C_6H_8O_7$ and $C_2H_2O_4$, respectively. In all cases, the following trends can be noticed: - the highest recovery yields of Ge is received at the highest pH values, and as the pH decreased, the recovery yield also decreases; - the yield of Pb is constant at the same level regardless of pH (in the case of HCl it slightly decreases with decrease in pH; expect for $C_6H_8O_7$, when the precipitate completely dissolves at the lowest pH). In addition, for H_2SO_4 , HCl and $C_5H_8O_7$, η_{Zn} has a similar trend as η_{Ge} - also decrease as the pH decrease. For HCl , η_{As} is kept constant regardless of the pH (expect for $pH=10.91$, when it reaches the maximum). Recovery of Ga is noted for H_2SO_4 and HCl , with best results reached at low pH ($pH=3.64$ for H_2SO_4 and $pH=4.93-3.60$ for HCl). The highest η_{Ge} is noted for $C_2H_2O_4$ in the pH range 10.58-9.56 and is more than 60%, to decrease significantly to a dozen % as the pH decreases; for other acids, η_{Ge} are also achieved at the highest pH and amount 25-35%. Generally, it is not possible to selective separation of Ge from other elements by precipitation by changing the pH. For $C_2H_2O_4$, η_{As} is kept constant (40-45%) for pH range 10.58-7.56 and decrease linearly to several % for pH below 5.78.

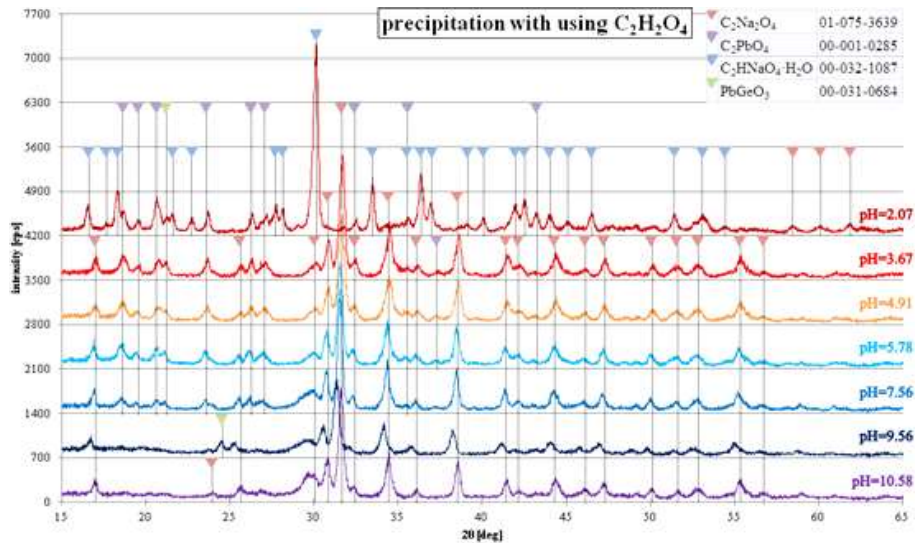


Fig. 4. XRD patterns of precipitates obtained by using $C_2H_2O_4$ at different pH

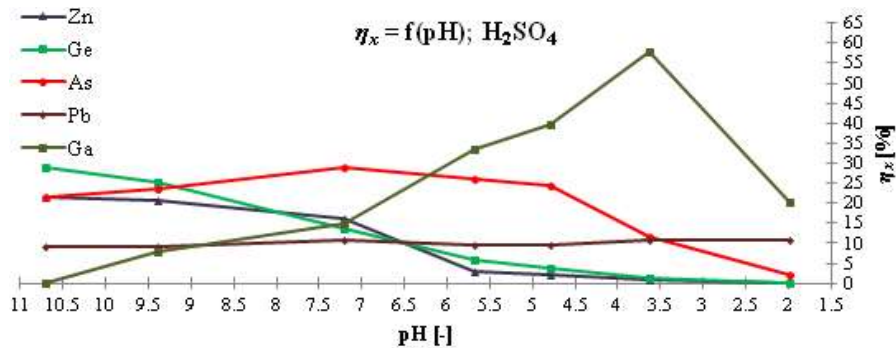


Fig. 5. Effect of pH value on recovery yield resulting from the use H_2SO_4

Comparison of recovery yields for industrial and synthetic solutions was made for H_2SO_4 , HCl and $C_6H_8O_7$ (Fig. 9, 10 and 11, respectively). Contents of Pb in both solutions were at similar level, so recovery yields should also be at a similar level at the same pH. Indeed, the absolute differences between $\eta_{Pb,IS}$ and $\eta_{Pb,SS}$ values are barely a few percentage points. While the content of Zn in SS was much higher than in IS, hence $\eta_{Zn,SS}$ should be lower than the corresponding $\eta_{Zn,IS}$. Contrary to expectation, it doesn't happen, while the η_{Zn} values for IS and SS are similar (in the case of H_2SO_4 , the absolute difference are slightly larger and are 3-6%). Due to the lower contents of Ge and As in SS, higher recovery yields of these elements for SS can be expected. This representation can be found in each case. The discrepancies between $\eta_{As,IS}$ and $\eta_{As,SS}$ are significant and amount to dozen-tens percentage points; only for H_2SO_4 at pH about 1.90 these values are at a similar level. For each acid, the differences between $\eta_{Ge,IS}$ and $\eta_{Ge,SS}$ are also significant, but decrease as the pH decreases. Generally, comparing the results of recovery yields of Ge and As for both solutions, it can be noticed that the lower the element concentration, the higher

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the recovery yield. Thus, solutions with low elements concentrations or diluted are suitable for recovery.

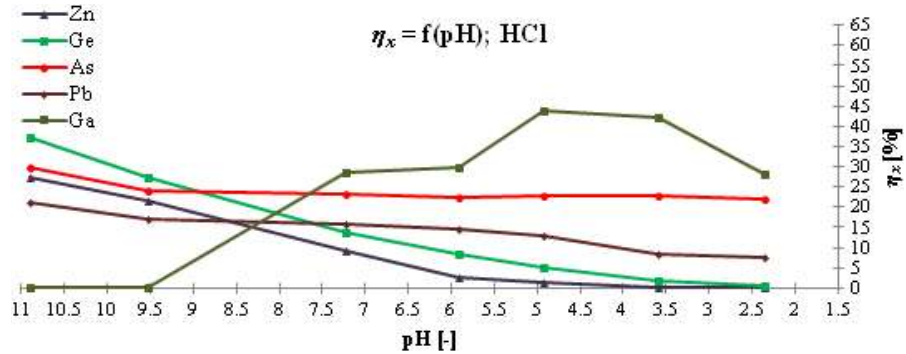


Fig. 6. Effect of pH value on recovery yield resulting from the use HCl

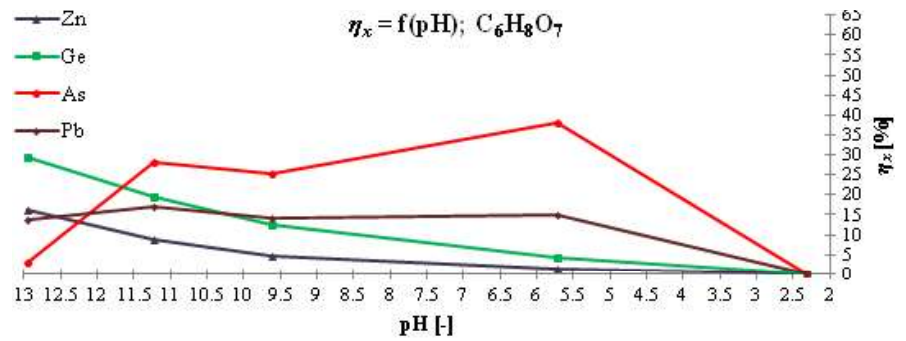


Fig. 7. Effect of pH value on recovery yield resulting from the use $\text{C}_6\text{H}_8\text{O}_7$

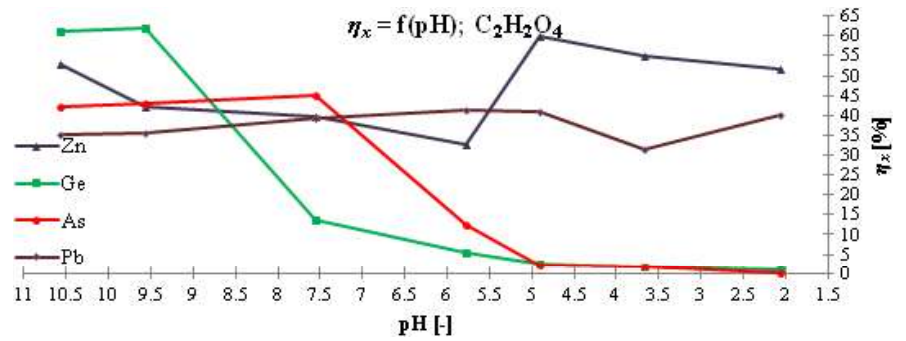


Fig. 8. Effect of pH value on recovery yield resulting from the use $\text{C}_2\text{H}_2\text{O}_4$

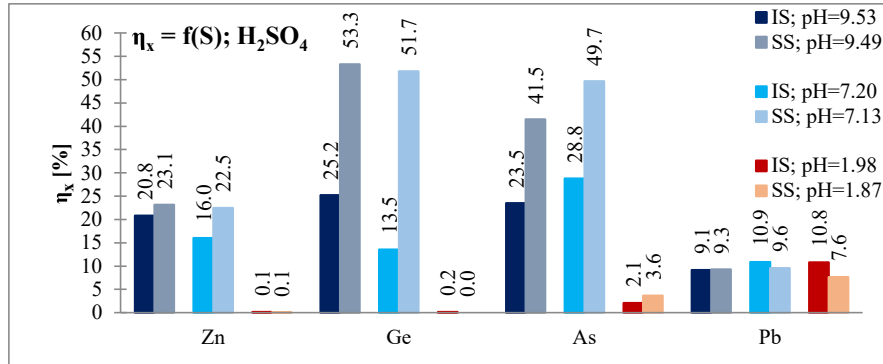


Fig. 9. Comparison of recovery yields for industrial and synthetic solutions, H_2SO_4

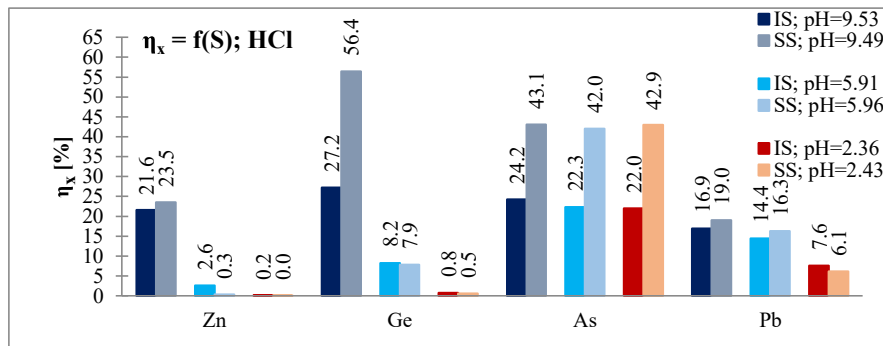


Fig. 10. Comparison of recovery yields for industrial and synthetic solutions, HCl

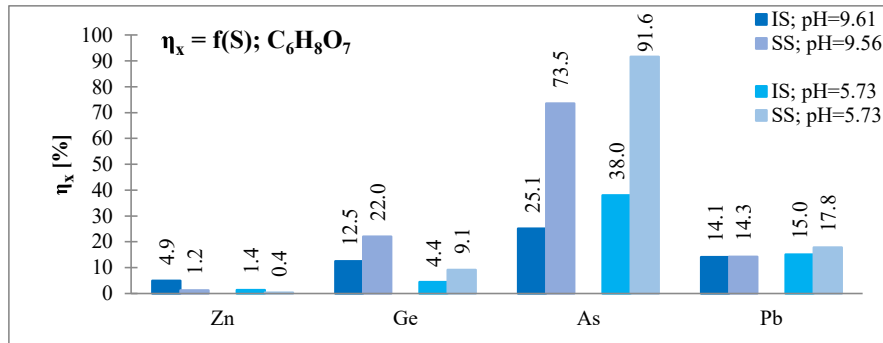


Fig. 11. Comparison of recovery yields for industrial and synthetic solutions, $C_6H_8O_7$

CONCLUSION

Germanium recovery process from an alkaline solution, which also contains other elements, especially heavy metal ions: Pb, As, Zn and other, by acidification is not the most effective method. This is because it does not allow for the selective recovery of germanium. However, it allows preparation of different phases

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depending on the acid, which was used and final pH of the solution. The higher the pH value, the recovery yield of germanium is higher. The highest recovery yield of germanium was received using oxalic acid, at pH 10.9-9.5, achieving a result of over 60%. Sulfuric and hydrochloric acids cause co-precipitation of gallium at low pH (approx. 3.6-4) which can be taken into account when considering the recovery of this element. Both industrial and synthetic solutions can be used for investigation. Comparing recovery yields received from industrial and synthetic solutions, it can be concluded that a lower concentration of germanium in solution results in a higher value of recovery yield.

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