Investigation of flotation of salts in their saturated solutions

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Abstract. Flotation of NaCl, KCl and KPF₆ in saturated aqueous solutions was investigated. The tests were carried out for salt particle sizes of >200, 100-200, 71-100 and <71 μm. Flotation tests were performed in a Hallimond flotation cell. In addition, contact angle was estimated using a flotometric method and measured by the sessile drop technique. The angles were 5 degree for NaCl and KCl and 8 degrees for KPF₆. Thus, there was mostly mechanical carryover of particles during the flotation test. However, an increase in the flotation yield of the tested salts with the increase of contact angle was observed.

1. Introduction
The aim of the research was to check the possible natural floatability of selected salts in their saturated aqueous solutions, i.e. to study salt flotation of salt. Commonly salt flotation studies concern flotation of minerals in aqueous salt solutions of various concentrations. As is known that, for substances that are naturally hydrophobic, salt flotation can be used in which there is no need for collecting reagents. Many researchers showed that salt influences the flotation of naturally hydrophobic particles [1]. There are works showing deterioration of salt flotation, especially at salts concentrations below 0.1 M [2-5]. This phenomenon is probably due to the increase in the surface charge of the particles, resulting in a decrease of the interfacial energy at the solid boundary and the aqueous solution of the salt. The decrease of this energy is responsible for reducing the contact angle and thus the deterioration of the flotation. There is usually improvement of the salt flotation at higher salt concentrations [4-9]. This is due to the surface tension of the aqueous solution. The improvement is observed for salts which surface energy is higher than the surface tension of water [1].

Recently, numerous studies on salt flotation were carried out on copper-bearing shale [10-13]. It results from the paper of Kurkiewicz and Ratajczak [14], that the hydrophobicity of copper-bearing shale increases with the concentration of NaCl in the aqueous solution. Smolska and Ratajczak [15] stated that the yield of copper-bearing shale flotation increases along with the surface tension of the aqueous salt solution. Kuklińska and Ratajczak [16] confirmed the influence of salt type and concentration on salt flotation of copper-bearing shale. Salt flotation tests were also conducted by Skowrońska and Drzymała [17], who found that the surface tension for the tested concentrations did not affect shale flotation. Bajek and Ratajczak [18] showed that the higher the concentration of salt, the better the flotation. Also, in the paper by Papmel and Ratajczak [19], it was found that along with the increase in the concentration of KCl salt, the yield in the copper-bearing shale concentrate is increasing.
2. Materials and methods
Flotation tests were carried out using NaCl, KCl and KPF₆, having particle size >200, 100-200, 71-100 and <71μm. Particle fractions of the tested substances were obtained using a laboratory ceramic mortar and a set of sieves with mesh sizes of 200, 100 and 71μm. Directly before the flotation process, each sample was wetted for 2 minutes with a saturated solution of a given salt and subjected to flotation in a Hallimond cell, which volume was 220 cm³ and height 36 cm.

Saturated solutions of salts (NaCl, KCl, KPF₆) were prepared on the basis of solubility data [20-25] and experimental testing of the amount of salt dissolved (Table 1). Each of the three solutions was made by dissolving the given amount of salt in 220 cm³ of distilled water and mixing with a magnetic stirrer for 5 minutes at 500 rpm. The tests were carried out at room temperature 25°C.

| Property | NaCl | KCl | KPF₆ |
|----------|------|-----|------|
| salt weight needed to prepare a saturated solution, g | 68.48 | 61.37 | 20.46 |
| concentration of saturated solution, M | 5.32 | 3.74 | 0.50 |

For the carried out flotation test, the amount of salt representing 100% yield depended on size of particles and is given in Table 2.

| Size of particles, μm | NaCl, g | KCl, g | KPF₆, g |
|----------------------|---------|--------|---------|
| >200                 | 2.55    | 2.16   | 2.81    |
| 100-200              | 2.38    | 2.03   | 2.44    |
| 71-100               | 1.99    | 1.41   | 1.78    |
| <71                  | 1.22    | 1.28   | 1.41    |

Flotation was carried out with an air flow of 2.5 dm³/h. Flotation time was up to 30 min. When the yield was constant for a long period of time, then the test was terminated.

3. Results and discussion
Flotation kinetics
Figures 2 (a-c) show flotation kinetics of NaCl, KCl and KPF₆ in their saturated solutions. The solid line illustrates the approximation of the obtained results with the first order kinetic curve equation (1) [26-28]:

\[ \gamma = \gamma_{\text{max}} (1 - \exp(-kt)) \]

where:
- \( \gamma \) – yield, %,
- \( \gamma_{\text{max}} \) - maximum yield, %,
- \( k \) – first order flotation rate constant, 1/min,
- \( t \) - time of flotation test, min.

The values of \( k \), \( \gamma_{\text{max}} \) and correlation coefficient \( R^2 \) are given in Table 3.

| size of particles, μm | NaCl, g | KCl, g | KPF₆, g |
|----------------------|---------|--------|---------|
|                     | \( k \), min⁻¹ | \( \gamma_{\text{max}} \), % | \( R^2 \) | \( k \), min⁻¹ | \( \gamma_{\text{max}} \), % | \( R^2 \) | \( k \), min⁻¹ | \( \gamma_{\text{max}} \), % | \( R^2 \) |
| >200                 | 0.0010 | 0.0914 | 0.0914 | 0.0914 | 0.1044 | 0.0914 | 0.0914 | 0.1044 | 0.0914 |
| 100-200              | 0.1034 | 0.9814 | 0.1052 | 0.1052 | 0.9760 | 0.1052 | 0.1052 | 0.9760 | 0.1052 |
| 71-100               | 0.1035 | 0.9814 | 0.1052 | 0.1052 | 0.9760 | 0.1052 | 0.1052 | 0.9760 | 0.1052 |
| <71                  | 0.1023 | 0.9814 | 0.1052 | 0.1052 | 0.9760 | 0.1052 | 0.1052 | 0.9760 | 0.1052 |
Figures 1 (a-c) show that the flotation yields of the tested salts are the highest for particle classes below 100 μm. In the case of NaCl (Fig. 1a), the yield for particle size fractions 0-71 μm and 71-100 μm is very similar. The largest observed yield was 67%. For the NaCl particles greater than 200 μm, there was no yield. The yield was constant after about 15 minutes from the start. In the case of KCl (Fig. 1b), the highest yield was obtained for the particle size below 100 μm at the level of 83%. As in the case of NaCl, for KCl with a particle size above 200 μm there was no yield. However, for KPF₆ (Fig. 1c) 100% the yield for the 71-100 μm size fraction was obtained after 21 minutes. Slightly smaller, 98% yield, was obtained for 0-71 μm particles. For >200 μm KPF₆ particles the yield was 20%. The highest yield for each particle size fraction was for KPF₆, followed by KCl and NaCl, as shown in Figure 2.
Figure 2. Influence of salt type (NaCl, KCl, KPF$_6$) on yield in flotation tests in individual particle fractions a) >200 μm, b) 100-200 μm, c) 71-100 μm, d) <71 μm.

Contact angle

The contact angle of the tested salts was determined by the sessile drop and flotometric methods. In case of the first method, bases on placing a drop of saturated salt solution on the surface of the compressed test salt, it was observed that the drop spilled over the entire surface of the prepared salt pellet. It was assumed that the contact angle for each salt tested was near zero or zero degrees, which is also confirmed by the work of Drzymała [28] for NaCl.

Assuming that the observed yields were caused by flotation, not entrainment, the contact angle of the studied salts was determined by using the so-called equation flotometric theory [29, 30]:

$$r_{max} = \left(\frac{3\alpha}{2g(\rho_s-\rho_w)}\right)^{0.5} \cdot \sin\left(\frac{\theta}{2}\right), \quad (2)$$

where:
- $r_{max}$ - particle radius ($r_{max} = d_{50}/2$), mm, determined from the separation curve (Fig. 4),
- $\alpha$ - surface tension, mN/m,
- $g$ - acceleration due to gravity, cm/s$^2$,
- $\rho_s$ - density of substance, g/cm$^3$,
- $\rho_w$ - density of solution, g/cm$^3$.

The particle $r_{max}$ was determined on the basis of approximation of the maximum cumulative yield from the mean particle ($2r_{max} = d_{50}$) of salt (Figure 3). The resulting values are presented in Table 4.
Figure 3. Separation curve of salt.

Table 4. $r_{\text{max}}$ values determined form the separation curve (Fig. 4).

| Salt   | $r_{\text{max}}, \mu\text{m}$ |
|--------|------------------------------|
| NaCl   | 62.8                         |
| KCl    | 70.3                         |
| $\text{KPF}_6$ | 72.2                     |

Surface tension values for the saturated salt solutions were determined basing on the literature data (Fig. 4) [1] and were included in Table 5.

Figure 4. Change in surface tension of the electrolyte solution in relation to water.

Table 5. Surface tension of saturated salt solutions.

| Salt solutions | Concentration of solution, M | Surface tension, mN/m |
|----------------|------------------------------|-----------------------|
| NaCl           | 5.33                         | 84.11                 |
| KCl            | 3.74                         | 79.99                 |
| $\text{KPF}_6$ | 0.50                         | 72.15                 |
Table 6 shows densities of salts and their aqueous solutions. The densities of salts and solutions were adopted from the Physicochemical Guide [20] and CRC [21], while the density of the saturated solution of KPF₆ was determined using a densymeter (pycnometer).

Table 6. Densities of salts and their saturated solutions.

| Salt    | Density of salt, g/cm³ | Density of saturated solution, g/cm³ |
|---------|------------------------|------------------------------------|
| NaCl    | 2.16                   | 1.20                               |
| KCl     | 1.98                   | 1.16                               |
| KPF₆    | 2.55                   | 1.10                               |

The resulting values of the contact angle determined with Eq. 2 are shown in Table 7.

Table 7. Contact angle of salts tested.

| Salt    | Contact angle, θ,° |
|---------|--------------------|
| NaCl    | 4.95               |
| KCl     | 5.24               |
| KPF₆    | 7.63               |

The determined contact angles of the tested salts are small, at the level of 5-8°, and confirm great wettability of the surface of these salts. At the same time, the relationship between contact angle (Table 7) and yield of salt (Figure 2) is clearly visible, which is also shown in Figure 5. However, given the very poor hydrophobicity of the salts tested, the increase in flotation can be mostly attributed to the mechanical carryover [31].

![Figure 5](image-url)  
**Figure 5.** Influence of contact angle on yield flotation salts at particles size 71-100µm.

Comparing the two above methods for determining the contact angle, it can be stated that the flotometric method is much more accurate than the sessile drop. The sessile drop method is an optical procedure that is subject to human error because the human eye is unable to see such small angles.

When investigating the influence of salt density or saturated solutions and the surface tension of salt solutions on yield flotation, one can observe an explicit proportional dependence of salt density and yield (Fig. 6a) as opposed to saturated solution density (Fig. 6b) and surface tension (Fig. 6c).
Analyzing the results of flotation of the studied salts, it can be seen that the lower concentration of saturated salt solution the higher yields were obtained (Fig. 7). It also resulted in an increase in the process kinetics. KPF$_6$ salt has the highest kinetics of the process since the value of $k$ is 0.1810 l/min. For comparison, this parameter for KCl is 0.1052 l/min, and for NaCl 0.1035 l/min (Table 3).

**Figure 6.** Effect of density of: a) salt and b) saturated solutions; and c) surface tension of salt solutions on yield of salt for 71-100 μm particles size.

**Figure 7.** Effect of saturated solution concentrations on salt yield for 71-100 μm size fraction.
It should be added that the reason of differences in flotation of the investigated salts was not caused by the morphology of the salt particles because they were regular in shape (Fig. 8).

![NaCl, KCl, KPF₆](image)

**Figure 8.** Microscopic image of salts (100-200 μm) in their saturated solutions.

4. Conclusions

The work considered the effect of saturated solutions of salts, with different molar concentrations, on flotation kinetics of salts, and also took into account the influence of the size of particles (> 200, 100-200, 71-100, <71 μm) on the process kinetics. During the tests, it was found that the kinetics of the process, in addition to the factors mentioned above, is also affected by the salt density, surface tension of the salt and the contact angle. As a result of the research, it was found that:

- NaCl, KCl, KPF₆ are hydrophilic (sessile drop method, Figure 4) or very slightly hydrophobic (5-8°, flotometric method, Table 7), and their flotation is mostly the result of mechanical carryover,
- flotation of salt depends on type of salt, its contact angle, the surface tension of the salt solution and the density and size of the salt particles,
- as the molar concentration of the saline solution increases (Fig. 8), the yield of salt flotation decreases as well as the kinetics of the process. KPF₆ salt having the lowest molar concentration of the solution (0.5M) floated best, while the NaCl, whose molar concentration was over 5M, floated worst,
- larger particles cause much worse entrainment than the smaller ones (Figures 3a-d). Yield was the highest for the 71-100 and <71 μm particles. For KPF₆, 100% of the yield for 71-100 μm particles was achieved (Figure 3c),
- along with the increase in the density of the studied salt, the yield also increased (Fig. 7a), in contrast to the density of the salt solution (Fig. 7b),
- lower surface tension of salt improved salt yield (Fig. 7c),
- as the contact angle increased, the yield increased (Fig. 6, 8).

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Acknowledgements
The work was financed by the Polish Statutory Research Grant