

EXPERIMENTAL RESEARCHES OF AQUEOUS HIGHLY CONCENTRATED MULTICOMPONENT SALT SOLUTIONS TREATMENT METHODS

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It is spoken about features of aqueous highly concentrated multicomponent salt solutions treatment methods. It is also advised a complex technology of treatment such kind of solutions.

Keywords: methods of aqueous highly concentrated multicomponent salt solutions treatment, crystallization, atmospheric distillation, vacuum distillation, acid neutralization

Problem of separation of aqueous highly concentrated multicomponent solutions of sodium salts is very acute for JSC “Salavatnefteorgsintez” and its difficulty is caused by very similar water solubility indexes.

For the moment there is an excess of maximum permissible concentration of nonorganic sodium salts in treated sewage which dumped in Belaya river from waste water treatment unit of the enterprise. For reducing of concentration of sodium sulfates, nitrites and nitrates in dumped water it is required to reduce its content in waste water which goes to the treatment unit. One of main source of these salts in industrial sewage is highly concentrated bittern which is aqueous alkaline solution with content of sulfates – 30-100 g/dm³, nitrites – 3-70 g/dm³, nitrates – 30-60 g/dm³, sodium hydroxide – 0,5-3 % mass.

There were chosen next methods of bittern neutralization and utilization:

- crystallization;
- atmospheric distillation;
- vacuum distillation;
- reagent processing;
- complex processing.

Analytical control of bittern and treated water was made according to the methodologies that used in waste water laboratory of R&D centre of JSC «Salavatnefteorgsintez».

Bittern's crystallization

Isohydric crystallization. Processing was carried out with the temperature of 20, 10, 0 and minus 5 °C. Duration was one hour. Water losses at different temperatures were accordingly 90,9, 89,7, 90,8, 81,8 g.

Results are shown in table 1.

Table 1

Results of bittern's isohydric crystallization

| Temperature, °C | Item | Input/ Output | pH | Density, g/dm ³ | Concentration, g/dm ³ | | |
|-----------------|---------------------|---------------|-------|----------------------------|----------------------------------|------------------------------|------------------------------|
| | | | | | SO ₄ ⁻² | NO ₂ ⁻ | NO ₃ ⁻ |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| +20 | Initial bittern, ml | 1000,0 | 12,05 | 1,163 | 54,0 | 41,5 | 11,0 |
| | Filtrate, ml | 920,0 | 12,10 | 1,137 | 40,5 | 44,2 | 13,5 |
| | Solid residue, g | 26,0 | – | – | presence of all ions | | |

Table 1 continuation

| | | | | | | | |
|-----|---------------------|--------|-------|-------|----------------------|------|------|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| +10 | Initial bittern, ml | 1000,0 | 12,05 | 1,163 | 54,0 | 41,5 | 11,0 |
| | Filtrate, ml | 900,0 | 12,23 | 1,127 | 21,0 | 41,5 | 12,5 |
| | Solid residue, g | 59,0 | – | – | presence of all ions | | |
| 0 | Initial bittern, ml | 1000,0 | 12,05 | 1,163 | 54,0 | 41,5 | 11,0 |
| | Filtrate, ml | 915,0 | 12,25 | 1,115 | 20,5 | 44,2 | 14,7 |
| | Solid residue, g | 52,0 | – | – | presence of all ions | | |
| – 5 | Initial bittern, ml | 1000,0 | 12,05 | 1,163 | 54,0 | 41,5 | 11,0 |
| | Filtrate, ml | 920,0 | 12,28 | 1,110 | 15,2 | 43,5 | 14,6 |
| | Solid residue, g | 60,0 | – | – | presence of all ions | | |

Solid sediment in amount of 4-10 % mass of the initial bittern was obtained in all experiments in case of isohydric crystallization processing.

Concentration of sodium sulfate in filtrate is decreasing with reducing of temperature and became 15,2 g/dm³ with minus 5 °C (reduced on 72 %). Nitrates and nitrites weren't actually precipitated with these conditions.

Cascade crystallization. In order to intensify bittern's crystallization processing the cascade crystallization was used, where the filtrate from the previous stage goes to the next one. Process temperature is 7-10 °C, duration of each stage - correspondingly 20, 30, 60 minutes. Water losses were accordingly 57, 22, 19,6 g. Solid residue was separated from filtrate by using of vacuum filtration. Results are shown in table 2.

Table 2

Results of bittern's cascade crystallization

| Stage of crystallization | Item | Input/ Output, g | pH | SO ₄ ⁻² | NO ₂ ⁻ | NO ₃ ⁻ |
|--------------------------|------------------------------------|---------------------|------|-------------------------------|------------------------------|------------------------------|
| I | Initial bittern, g/dm ³ | 1163 | 12,5 | 54,0 | 11,4 | 41,5 |
| | Filtrate, g/dm ³ | 1083,0 | 12,1 | 40,5 | 11,7 | 44,2 |
| | Solid residue, % mass. | 23,0 | – | 78,1 | 12,4 | 9,5 |
| II | Filtrate, g/dm ³ | 1045 | 12,1 | 30,0 | 12,5 | 45,2 |
| | Solid residue, % mass. | 16,0 | – | 80,8 | 14,1 | 5,1 |
| III | Filtrate, g/dm ³ | 1021 | 12,2 | 27,0 | 13,0 | 46,5 |
| | Solid residue, % mass. | 4,4 | – | 82,5 | 14,3 | 3,2 |

As it shown in the table 2, sulfates concentration in bittern's filtrate is decreased by 50 % after 3rd stage of crystallization, nitrites and nitrates concentration is increased by 14 and 12 % correspondingly (don't take into account the losses of water phase).

There are also carried out the experiments in order to check the possibility of application of distillation methods for highly concentrated multicomponent salt solutions neutralization.

Atmospheric distillation

By using dephlegmator we try to distil off as much water as it possible and this water should satisfy the requirements for waste water dumping from plants to the waste water treatment unit or for technological purposes. Results are shown in table 3.

Table 3

Results of bittern's distillation with dephlegmator

| № | Item | Input/Output, ml | pH | SO ₄ ⁻² | NO ₂ ⁻ | NO ₃ ⁻ |
|---|------------------------------------|------------------|------|-------------------------------|------------------------------|------------------------------|
| 1 | Initial bittern, g/dm ³ | 1000 | 11,6 | 70,20 | 5,50 | 9,00 |
| | Distillate, g/dm ³ | 500 | 9,0 | absence | absence | absence |
| | Residue, % mass. | 500 | – | 83,46 | 6,63 | 9,91 |
| 2 | Initial bittern, g/dm ³ | 1000 | 11,7 | 78,00 | 4,90 | 9,60 |
| | Distillate, g/dm ³ | 700 | 9,0 | 0,02 | 0,20 | 0,60 |
| | Residue, % mass. | 300 | – | 86,21 | 4,84 | 8,94 |

In case of 50 % of distillate recovery (№1) there is practically no salts in it, they remain in residue. In case of 70 % of distillate recovery (№2) there is a presence of all initial salts in a small amount. It is most likely droplet entrainment in second case because of intensive heating of concentrated bittern.

Vacuum distillation

Vacuum distillation of bittern is carried out to the solid residue. In order to avoid droplet entrainment of sodium salts into distillate processing was carried out with temperature 60-65 °C, pressure was 100 torr. Losses were 4,72 % mass.

Results are shown in table 4.

Table 4

Results of bittern's vacuum distillation

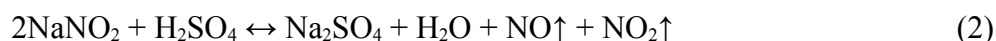
| Item | Output, % mass. | pH | SO ₄ ²⁻ | NO ₂ ⁻ | NO ₃ ⁻ |
|------------------------------------|-----------------|-------|-------------------------------|------------------------------|------------------------------|
| Initial bittern, g/dm ³ | 100,00 | 11,80 | 29,94 | 22,5 | 14,37 |
| Distillate, g/dm ³ | 71,52 | 7,00 | absence | absence | absence |
| Solid residue, % mass. | 23,76 | – | 45,32 | 34,54 | 20,15 |

As a result we have practically total absence of sodium salts in distillate.

Reagent processing

Reagent processing showed the inexpediency of its usage. Calcium hypochlorite, calcium hydroxide, ammonium hydroxide and other reagents were used. Processing was carried out with temperature 20, 40 and 60 °C and with various amounts of chemicals. Reagent processing of bittern didn't obtain considerable reducing of sulfates content. Residue amount is also increased with chemicals dosage increasing and at the same time sulfates content in filtrate isn't reduced significantly.

In order to reduce nitrites content bittern is also processed with concentrated sulfuric acid, in that case next reactions are assumed:



H₂SO₄ is added into bittern with permanent agitation, intensive gas release took place consequently, agitation is processed until gas release stopping. In 1st case dosage of acid was calculated, in 2nd case it was overdose.

Results are shown in table 5.

From the table data we can said that reactions 1, 2 takes place in both cases of neutralization processing of bittern.

Table 5

Results of bittern's neutralization

| Item | pH | Concentration, g/dm ³ | | |
|--|-------|----------------------------------|------------------------------|------------------------------|
| | | SO ₄ ⁻² | NO ₂ ⁻ | NO ₃ ⁻ |
| Initial bittern | 11,20 | 47,62 | 20,51 | 10,34 |
| Neutralized bittern 1 st case | 4,45 | 54,60 | 16,97 | 10,78 |
| Neutralized bittern 2 nd case | 0,7 | 80,95 | 2,83 | 10,87 |

Complex processing of bittern

Vacuum distillation of neutralized bittern. Processing is carried out with the same conditions to solid residue. Then thermal treatment of received residue is took place in order to eliminate nitrites.

Results are shown in table 6.

Table 6

Results of bittern residue's thermal treatment

| Temperature/pH of neutralized bittern | Concentration, % macc. | | |
|---------------------------------------|-------------------------------|------------------------------|------------------------------|
| | SO ₄ ⁻² | NO ₂ ⁻ | NO ₃ ⁻ |
| 150 °C/pH 0,7 | 88,07 | 0,97 | 10,97 |
| 385 °C/pH 0,7 | 89,49 | 0,74 | 9,78 |
| 150 °C/pH 4,45 | 72,78 | 14,26 | 12,96 |
| 385 °C/pH 4,45 | 73,57 | 13,74 | 12,68 |

Methods of reagent processing, crystallization and atmospheric distillation shows insufficient efficiency in terms of bittern's neutralization, therefore they wouldn't be recallable in conditions of sodium sulfate production. In case of reagent processing there were both small decreasing of sodium sulfate concentration and bringing in solution the additional amount of another salts. In case of crystallization we have only sodium sulfate decreasing to the certain level which is stipulated by its solubility. In case of atmospheric distillation we have only 50 % of pure distillate recovery and more concentrated residue which have worse pumpability and higher risk of crystallization inside the pipes.

Sequential application of neutralization, vacuum distillation and thermal treatment methods will allow us to receive the solid residue of salts which could satisfy

the product's technical requirements with admixing of obtained salts and main stream of commercial sodium sulfate in right dosage. Received distillate (80 % distillate recovery) could be used for technological purposes. We can also find an application of this salt in other areas, for example, in glasswork, pulp-and-paper or chemical industries.

Thus the most efficient way to settle the problem of neutralization and utilization of aqueous highly concentrated multicomponent salt solutions is the combined technology which will allow us to solve the ecological problems of the enterprise, to receive commercial product and to renew consumed water sources.

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