

EXTRACTION OF LITHIUM BY ORGANIC SOLVENTS

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ABSTRACT

In this paper, the extraction of lithium using methanol as an organic solvent has been discussed. Lithium is present in the water of Pachbhdra, Didewana and Nawa City. It was found that the methanol is an excellent solvent. Pachbhdra brine is best suited as it contains 70 ppm lithium. Methanol enriched the lithium values and extracted 57.18% lithium and suppressed sodium and potassium to 4.3% and 21.00% lithium, respectively.

Key words : Extraction, Lithium, Organic solvents

INTRODUCTION

The important methods for recovery of metals from the area and minerals have been pyrometallurgy and hydrometallurgy. These two important techniques dominated the metallurgical process for centuries. However, owing to the dwindling up of the richer sources and sulphide ores of acceptable grade have compelled the metallurgists to modify the wet methods of processing of lean ores, minerals, slimes and tailing till 1970. The recovery of the trace metals present in the ore was over looked and were generally rejected in common methods practiced in hydrometallurgy as well as pyrometallurgy. The quest for rare mineral and rare elements of present day high technology has given birth to the development of the solvent extraction technology, which is a successful technique in recovery of trace metals and rare elements.

Solvent extraction in metallurgical process

The large scale application of the solvent extraction for recovery, separation and purification is only half a century old. As early as 1942, diethyl ether was used for the extraction of uranyl nitrate with remarkable success. However, the low boiling point and high inflammability of diethyl ether was not suitable for plants as its involves the risk. There after a number of solvents with better physical properties, high extractive power and low cost were discovered. These includes –

- (i) TBP [Tri-n-butyl phosphate]
- (ii) D₂EPA [di (2-ethyl hexyl) – phosphoric acid]
- (iii) TOPO [Tri octyl phosphine oxide]

(iv) R_3N [Tri octyl amine]

A number of trace metals of considerable importance in area of micro electronics and material science were also desired to be obtained through economically viable methods and in this field also, solvent extraction as a unit operation was highly successful. The metals like zirconium, rare earth, indium, gallium, niobium and tantalum, required in high technologies, were obtained in high purity and large quantities, which could not be achieved earlier by metallurgist by conventional methods.

In some of the metallurgical processes utilising wet methods of extraction, significant amount of trace metals of commercial importance are produced. These metals can be extracted through solvent extraction technology. Quite recently M/S Hindustan Zinc Ltd., Udaipur (HZL) has developed a solvent extraction process for extraction of cobalt present in the zinc processing waste. The cake containing trace quantity of cobalt is stock-piled and cobalt is extracted with D_2EPA [di(2-ethyl hexyl)-phosphoric acid]. The process was developed in joint collaboration with Bhabha Atomic Research Center and HZL Central Research and Development Laboratory, Udaipur during 1984-88 and plant is in operation.

Solvent extraction process

The extraction of the metals with non-polar solvents is unexpected. Most of the metals salts being strong electrolytes are ionic in nature and exhibit relatively high solubility in aqueous media in which the ions are solvated by water molecules. In general the extraction process

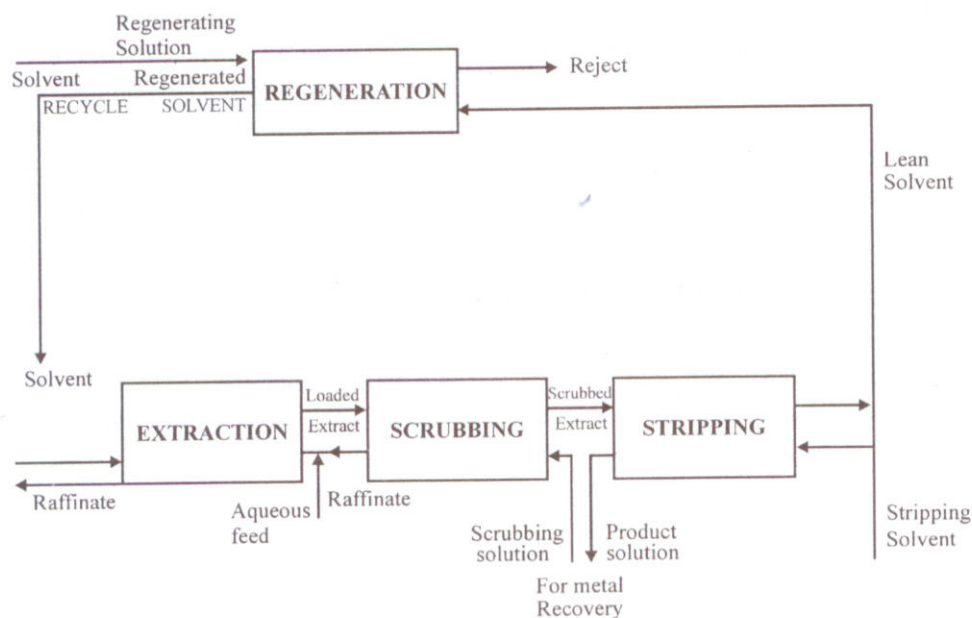


Figure 1. General flow-sheet of a sx process

involves the four separate operations : (i) Extraction, (ii) Scrubbing, (iii) Stripping, (iv) Regeneration of solvent.

Preinvestigated solvent extraction method for lithium

The method which is most widely used for the extractive separation of lithium from sodium and potassium ions as well as from other alkali metals is based on the solubility of lithium chloride in oxygen-containing organic solvents, such as the aliphatic alcohols, ketones and ethers, in the presence or absence of dry hydrogen chloride. Under these conditions, the other alkali metals are rather insoluble in these solvents provided that they are present as the dry chlorides and the solvent used for extraction contains as little water as possible. The n-propanol, iso-propanol, n-pentanol, 2-ethyl hexanol, acetone, cyclohexane, dioxane and mixtures of diethyl ether with absolute ethanol¹⁰ have been recommended as extractants for the lithium chloride.

The dry mixture of the chlorides of lithium and the other alkali metals is equilibrated with the anhydrous extractant, or the separation is carried out using an apparatus for continued extraction.

Because many other elements such as iron, gallium, molybdenum etc. are co-extracted with the lithium, this extraction method is of very limited applicability. In most cases, it can be only carried out after preliminary separation of lithium and other alkali metals by means of other procedures. Besides, there is always the possibility that some of the sodium ions may pass into the organic phase, especially when present in great quantities. Thus, about one percent of sodium is co-extracted, when the lithium chloride is extracted with isopropyl.

Present method

The lithium has been reported in ground waters in India. Deshpande¹² has reported the presence of 4.0 ppm lithium in ground water of Partiala area of Kirshana District probably derived from the mica in the biotite genesis.

Significant contribution in exploration of lithium values in surface and well waters of Rajasthan has earlier been reported from this laboratory by Menaria and Hussain¹⁰. It was discovered that the brine sample from a well in Nawa city contained lithium of the order of 80 ppm, which is considered economical viable for extraction of lithium as per international norms for lithium industry. Inspired by this significant discovery, extensive survey and analysis of various salt lakes and brine well water was carried out covering the entire belt of geologically similar.

The systematic survey of the water samples from Pachbhdra, Nawa and Didewana were carried out. The analysis has been reported in Table 1.

In order to extract lithium values, the solvent extraction technique was used and accordingly following solvents were used.

Table 1. Indian Brine

| SOURCE | Composition (ppm) | | | | | | |
|------------|-------------------|-----------------|----------------|------------------|------------------|------------------------------|-----------------|
| | Li ⁺ | Na ⁺ | K ⁺ | Co ⁺² | Mg ⁺⁺ | SO ₄ ⁺ | Cl ⁻ |
| NAWA | 47 | 110000 | 700 | 700 | 3860 | 20000 | 155845 |
| DIDEWANA | 30 | 68000 | 250 | 200 | 84 | 34000 | 68160 |
| PACHBHADRA | 70 | 150000 | 36000 | 2000 | 41000 | 35000 | 35000 |

Table 2. Chemicals used in extraction with organic solvents

| | |
|--------------------|------------------------------------|
| 1. Methanol | L.R. s.d. Fine Chem. Ltd., Bombay |
| 2. Ethanol | Riedel de Haem, Switzerland |
| 3. Propanol | L.R. s.d. Fine Chem. Ltd., Bombay |
| 4. Butanol-1 | I.P. Vitermike Pharma, Ltd. Nadiad |
| 5. 2-Ethyl Hexanol | I.P. Asses Chemicals, Jodhpur |
| 6. Acetone | L.R. Sarabhai M. Chem., Baroda |
| 7. 1, 4-Dioxane | L.R. Sarabhai M. Chem., Baroda |
| 8. Pyridine | L.R. s.d. Fine Chem. Ltd., Bombay |

EXPERIMENTAL

Brine sample was drawn from Nawa city (District Nagaur), Pachbhadra city (District Barmer) and Didewana (District Nagaur) in Western Rajasthan. 100 mL of brine sample was evaporated to dryness and carefully transferred to 250 mL round bottom flask, fitted with reflux condenser and 50 mL solvent was added. The mixture was heated over a water bath and refluxed for 30 minutes. In case of pyridine and 2-ethyl hexanol, a sand bath was used.

The flask was cooled and supernatant was transferred to 100 mL round bottom flask, about 25 mL solvent was further added and again refluxed for 30 minutes and the supernatant was transferred to 100 mL flask containing the lithium extracted earlier. The process was again repeated with 25 mL of solvent and transferred to 100 mL flask. The total volume of the extract was transferred to a distillation flask and solvent was recovered. The dry mass left after removal of the solvent by distillation was extracted in distilled water and solution was made up to 100 mL. This 100 mL solution was analysed for lithium, sodium and potassium. Results are reported in Tables 3, 4, 5 and 6, respectively.

Table 3. Solvent extraction values from Nawa brine

| S.No. | Solvent | Composition of solvent extract from brine residue (ppm) | | | Percentage extracted | | |
|-------|-----------------|---|-----------------|----------------|----------------------|-----------------|----------------|
| | | Li ⁺ | Na ⁺ | K ⁺ | Li ⁺ | Na ⁺ | K ⁺ |
| 1. | Methanol | 20 | 5000 | 200 | 42.65 | 4.5 | 28.5 |
| 2. | Ethanol | 15 | 4800 | 155 | 31.9 | 4.3 | 22.1 |
| 3. | Propanol | 08 | 3600 | 135 | 14.0 | 3.2 | 19.2 |
| 4. | Butanol-1 | 57 | 3420 | 120 | 11.0 | 3.1 | 17.1 |
| 5. | 2-Ethyl hexanol | 05 | 2500 | 130 | 10.6 | 2.2 | 18.5 |
| 6. | Acetone | 07 | 2300 | 140 | 14.8 | 2.09 | 21.45 |
| 7. | 1, 4-Dioxane | 06 | 2700 | 145 | 12.76 | 2.45 | 20.7 |
| 8. | Pyridine | 10 | 3500 | 160 | 21.2 | 3.18 | 22.8 |

Table 4. Solvent extraction values from Didewana brine

| S.No. | Solvent | Composition of solvent extract from brine residue (ppm) | | | Percentage extracted | | |
|-------|----------------|---|-----------------|----------------|----------------------|-----------------|----------------|
| | | Li ⁺ | Na ⁺ | K ⁺ | Li ⁺ | Na ⁺ | K ⁺ |
| 1. | Methanol | 18 | 4000 | 70 | 60 | 5.8 | 28 |
| 2. | Ethanol | 10 | 3200 | 75 | 33.3 | 4.7 | 30 |
| 3. | Propanol | 07 | 2400 | 45 | 23.3 | 3.5 | 18 |
| 4. | Butanol-1 | 03 | 2700 | 49 | 10 | 3.9 | 19.6 |
| 5. | 2-Ethyl exanol | 02 | 1800 | 41 | 6.6 | 2.6 | 16.4 |
| 6. | Acetone | 05 | 2100 | 32 | 16.6 | 3.2 | 12.8 |
| 7. | 1, 4-Dioxane | 04 | 2300 | 36 | 13.3 | 3.38 | 14.4 |
| 8. | Pyridine | 09 | 2500 | 39 | 30 | 3.67 | 15.6 |

Table 5. Solvent extraction values from Pachbhadra brine

| S.No. Solvent | Composition of solvent extract from brine residue (ppm) | | | Percentage extracted | | |
|-------------------|---|-----------------|----------------|----------------------|-----------------|----------------|
| | Li ⁺ | Na ⁺ | K ⁺ | Li ⁺ | Na ⁺ | K ⁺ |
| 1. Methanol | 40 | 6500 | 756 | 57.18 | 4.3 | 21.0 |
| 2. Ethanol | 32 | 5720 | 786 | 45.71 | 3.81 | 21.8 |
| 3. Propanol | 18 | 5230 | 504 | 25.7 | 2.5 | 14.0 |
| 4. Butanol-1 | 10 | 5550 | 842 | 14.2 | 3.7 | 23.3 |
| 5. 2-Ethyl exanol | 06 | 1988 | 490 | 8.5 | 1.3 | 13.6 |
| 6. Acetone | 04 | 4860 | 980 | 5.71 | 3.2 | 27.2 |
| 7. 1, 4-Dioxane | 12 | 2969 | 560 | 17.14 | 1.79 | 15.27 |
| 8. Pyridine | 15 | 3435 | 675 | 21.42 | 2.29 | 18.54 |

Table 6. Extraction of lithium by organic solvents

| S.No. Solvent | Percentage of lithium | | | | | | | | |
|--------------------|-----------------------|---------------|------------------------|----------------|---------------|------------------------|------------------|---------------|------------------------|
| | Nawa brine | | | Didewana brine | | | Pachbhadra brine | | |
| | Organic layer | Aqueous layer | % of lithium extracted | Organic layer | Aqueous layer | % of lithium extracted | Organic layer | Aqueous layer | % of lithium extracted |
| 1. Methanol | 0.002 | 0.0025 | 42.5 | 0.0018 | 0.0011 | 60 | 0.004 | 0.0027 | 57.1 |
| 2. Ethanol | 0.0015 | 0.0031 | 31.9 | 0.0010 | 0.0019 | 33.3 | 0.0032 | 0.0035 | 45.7 |
| 3. Propanol | 0.0010 | 0.0035 | 21.2 | 0.0009 | 0.002 | 30 | 0.0015 | 0.0054 | 21.4 |
| 4. Butanol-1 | 0.0007 | 0.0038 | 14.8 | 0.0005 | 0.0021 | 16.6 | 0.0004 | 0.0065 | 5.7 |
| 5. 2-Ethyl hexanol | 0.0008 | 0.0037 | 17.0 | 0.0007 | 0.002 | 23.3 | 0.0018 | 0.0051 | 25.7 |
| 6. Acetone | 0.0006 | 0.0040 | 12.7 | 0.0004 | 0.0025 | 13.3 | 0.0012 | 0.0056 | 17.1 |
| 7. 1, 4-Dioxane | 0.00052 | 0.0041 | 11.0 | 0.0003 | 0.0025 | 10 | 0.0001 | 0.0059 | 14.2 |
| 8. Pyridine | 0.0005 | 0.0041 | 10.6 | 0.0002 | 0.0027 | 6.6 | 0.0006 | 0.0062 | 8.5 |

RESULTS AND DISCUSSION

The recovery of lithium from the brine and saline waters of western Rajasthan was discovered in our laboratory. This is the first investigation, which has reported the presence of the micronutrient lithium in the salts obtained from salt lakes of Rajasthan. These lakes are major sources of table salt supply for the state of Rajasthan, Punjab, U.P., Haryana and M.P. Though it was well recognised that the salt from Pachbhadra is nutritionally far better than the salts from Sambhar, Nawa and Didewana and also from marine. The superiority of Pachbhadra

salt over other sources was established, though exact composition was not known. The salts obtained from Sambhar, Nawa and Didewana were ranked below the quality of Pachbhadra salt only on the basis of colour and texture. It will be relevant to mention here that the quality of Sambhar salt deteriorates due to algal growth in the shallow water of the lake. The algal growth on the salt imparts blue-green and mostly pink colour to the salt produced by its own conventional method. The quality of salt from Didewana is also not good for many reasons, as it includes high percentage of the sulphate, which spoils the taste and the quality. Furthermore, sulphur reducing bacteria converts the sodium sulphate partly into sodium sulphide imparting a black colour and foul smell of H_2S in area of salt mining. The salt from Didewana is generally a preferred chemical for leather tanning industry rather than as the table salts. The salt from Nawa city is comparatively of good quality with less amount of sodium sulphate and high percentage of sodium chloride. The brine is taken out from the wells and a good quality of sodium chloride obtained, which is suitable as the industrial sodium chloride. For chlor-alkali industry, the salt is being manufactured by a number of industries with modern technologies but still the worth of Nawa salt, a salt rich with micronutrient lithium is still obscure. The micronutrient lithium has excellent characteristics for central nervous system (C.N.S.) and gives its consumer protection from psychic disorder related to different types of neurosis.

The Pachbhadra salt separates out in the best form. During solar evaporation of brine, magnesium chloride and calcium sulphate are separated in natural process of crystallisation, as adopted in age-old methods of salt manufacture in this area. There are yet other sources of salt in western Rajasthan, which includes Phalodi area. The quality of sodium chloride from brine from Phalodi wells is excellent and with rude techniques, very high quality product of the order of 98.5 to 99.5 sodium chloride is obtained, but Phalodi salt is kept out of the scope of the present studies, which is targeted for recovery of the mineral values in addition to sodium chloride present in salts, precisely the micronutrient lithium.

In the light of the above discussion and results, a comparative evaluation of Nawa, Didewana and Pachbhadra salts reveals that –

- (i) The quality of Pachbhadra salt is best as contaminants viz S^{2-} , SO_4^{2-} , algae are very low.
- (ii) The lithium present in these brines are, Nawa 47 ppm, Didewana 30 ppm and Pachbhadra 70 ppm. So the quality of Pachbhadra salt is best from nutritional point of view.
- (iii) Owing to the very low percentage of sodium sulphate and magnesium chloride, the colour texture and free flow quality of the Pachbhadra salt is maintained. It is also significant here to mention that during crystallisation the magnesium in common salt is highly suppressed.
- (iv) The solvent extraction experiments were performed in involving solid-liquid extraction. For extraction, the following solvents were used –

1. Methanol
2. Ethanol
3. Pyridine
4. Acetone

- | | |
|-------------|--------------------|
| 5. Propanol | 6. 1,4-Dioxane |
| 7. Butanol | 8. 2-Ethyl hexanol |

It was found that the methanol is an excellent solvent. Pachbhadra brine is best suited as it contains 70 ppm lithium. Methanol enriched the lithium values and extracted 57.18% lithium and suppressed sodium and potassium to 4.3% and 21.00% lithium, respectively.

- (v) The solvent extraction can be used for preconcentration of lithium value from other alkali metals viz sodium and potassium to a level of above 5000 ppm in solids for which technologies are available.

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