

Fig 3. SEM images of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ precipitated from subsoil brine using different additives (a) Na_2SO_4 (anhydrous) (b) Silicate industry effluent (c) Sambhar dried bittern (d) No additive.

Common salt (NaCl) fractions were collected between densities 25 to 28.5°Bé . The analysis (Table 4) indicates that purity of salt is increased from 97 wt.% to higher than 97.5 wt.% after treating the sub-soil brine with additives.

Table 4: Quantity and quality of salt crystallized between 25 to 28.5°Bé .

Additives	$^\circ\text{Bé}$	Salt weight (g)	NaCl %(w/w)
Na_2SO_4 (anhydrous)	25.15 – 28.4	5500	97.57
Silicate industry effluent	25.48 - 28.30	5336	97.71
Dried bittern	25.37 – 28.52	5523	97.78
Untreated	24.95 – 28.28	5750	97.00

The quality of the salt could be further improved by simple washing with the water to a purity level of 98.6 wt.%, which matches with the quality specified for industrial grade salt. The analysis of washed salt (ionic and probable composition) is given in Table 5. P-XRD pattern and FTIR spectra of unwashed and washed samples (Fig 4 a-d) indicate an improvement in quality of salt after washing.

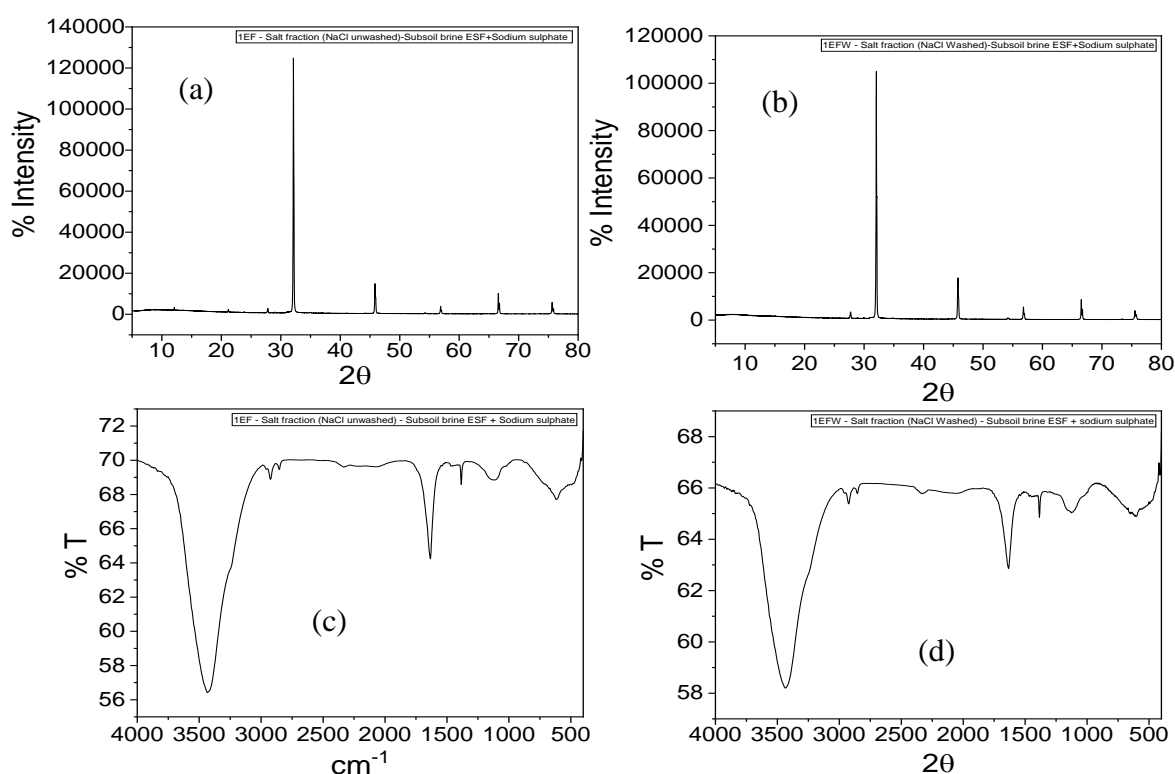


Fig 4. Representative P-XRD pattern of (a) unwashed (b) washed and FTIR spectra of (c) unwashed (d) washed sodium chloride obtained using an additive in sub-soil brine.

Table 5: Ionic and probable composition of washed salt.

	Ca ⁺⁺ % (w/w)	Mg ⁺⁺ % (w/w)	SO ₄ ⁻ % (w/w)	Cl ⁻ % (w/w)	K ⁺ % (w/w)
Ionic composition	0.20	0.14	0.59	56.67	0.03
	CaSO ₄ % (w/w)	MgSO ₄ % (w/w)	MgCl ₂ % (w/w)	KCl % (w/w)	NaCl % (w/w)
Probable composition	0.70	0.15	0.46	0.05	98.62

Solar evaporation of sub-soil brine and sub-soil brine with additives was further carried out up to 34°Bé. Crude salts containing higher 96 wt. % NaCl purity in each case were obtained between 28.5 to 34°Bé (Table 6). The quality of such a salt could be further upgraded by simple washing to meet specifications of edible grade salt.

Table 6: Quantity and purity of salt recovered between 28.5 to 34.0°Bé.

Name	°Bé	Salt weight (g)	NaCl (% w/w)
Treated with Na ₂ SO ₄ (anhydrous)	28.40- 34.0	746	97.19
Treated with silicate industry effluent	28.30 – 34.0	870	96.49
Treated with dried bittern	28.52 – 34.0	953	96.57
Untreated	28.28 – 34.0	355	96.58

As calcium ions are mostly precipitated in the presence of sulphate or carbonate (Table 1), the remaining liquor (bittern) can be considered as a reciprocal quinary type with sodium, potassium, magnesium, chloride, and sulphate in water.

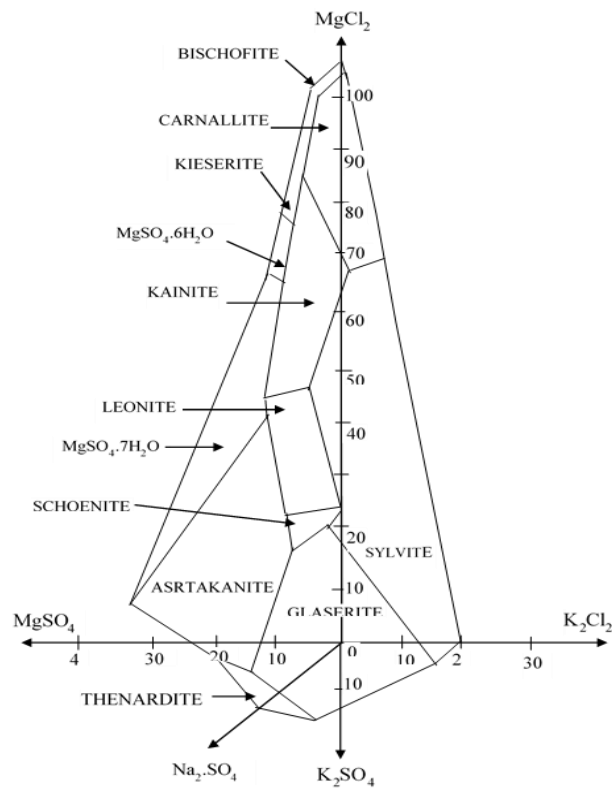


Fig 4. Quinary Diagram of Oceanic Salt system at 25°C, mol/1000 moles H₂O saturated with NaCl. (Reproduced from Ph. D. Thesis of Dr. Rohit H. Dave, 2006)

The equilibria between different phases of such a system is investigated by several researchers [34-40]. Simple representation of the oceanic salt system (Fig 4) based on van't Hoff data can be interpreted easily for the recovery of marine chemicals. After separation of crude salt, the filtrate was further analysed and evaporated to obtain mixed salts. The composition of bittern indicated formation of Carnallite for untreated sub-soil bittern (Fig 4) in a density range between 34.0 to 37.5°Bé. Formation of Kainite phase for treated sub-soil bitterns was seen from 35.5 to 37.5 °Bé. Therefore, mixed salts were recovered in two fractions (Table 7).

Table 7: Quantity and purity of mixed salts recovered between 34.0 to 35.5 °Bé 28.5 to 34.0 °Bé and 35.5 to 37.5 °Bé.

Name	Salt weight (g)	MgSO ₄ % (w/w)	MgCl ₂ % (w/w)	KCl % (w/w)	NaCl % (w/w)
Fraction I (34.0 to 35.5°Bé)					
Treated with Na ₂ SO ₄ (anhydrous)	219	28.12	3.87	12.42	38.08
Treated with silicate industry effluent	92	9.95	2.58	2.5	79.30
Treated with dried bittern	88	10.12	1.72	0.87	83.70
Untreated	310	0.60	42.66	28.50	4.60
Fraction II (35.5 to 37.5°Bé)					
Treated with Na ₂ SO ₄ (anhydrous)	218	36.86	3.44	19.26	17.93
Treated with silicate industry effluent	360	37.91	5.36	19.66	14.73
Treated with dried bittern	320	38.15	4.30	19.70	17.44
Untreated	52.41	0.60	32.45	20.38	5.46

P-XRD pattern (Fig 5 a-c) indicate formation of Kainite type salt whereas untreated brine produces Carnallite type of salt (Fig 5 d). Formation of Kainite was confirmed by matching with the standard data available (JCPDS file no. 74-0383) [41] The values of lattice parameters for the Carnallite crystals (Fig 5 d) are found to be in good agreement with the reported literature [42,43]. Formation of Kainite (Fig 6 a-c) and Carnallite (Fig 6d) type mixed salts was also confirmed from FTIR spectra. In Figs 6a-c, the broad band at 3300 cm^{-1} and the weak band at 1640 cm^{-1} are attributed to the stretching and bending modes of the lattice water. Two prominent bands at 1105 and 615 cm^{-1} correspond to different modes of the SO_4^{2-} in K_2SO_4 . Weak band observed around 748 cm^{-1} can be assigned to the wagging mode in H_2O of the crystal [44]. A comparison of FTIR spectra (Fig 6 d) with literature confirms high purity of precipitated Carnallite [45].

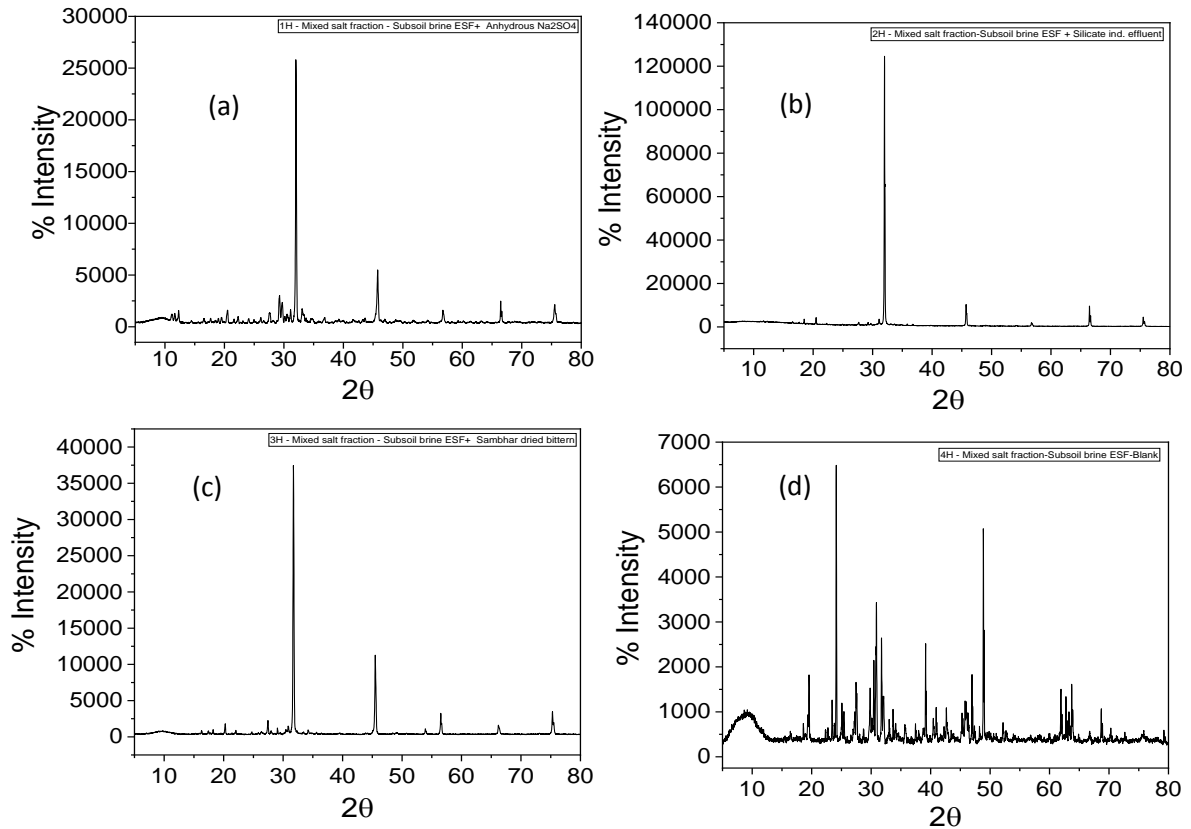


Fig 5. P-XRD pattern of mixed salts precipitated from subsoil brine using different additives (a) Na_2SO_4 (anhydrous) (b) Silicate industry effluent (c) Sambhar dried bittern (d) No additive.

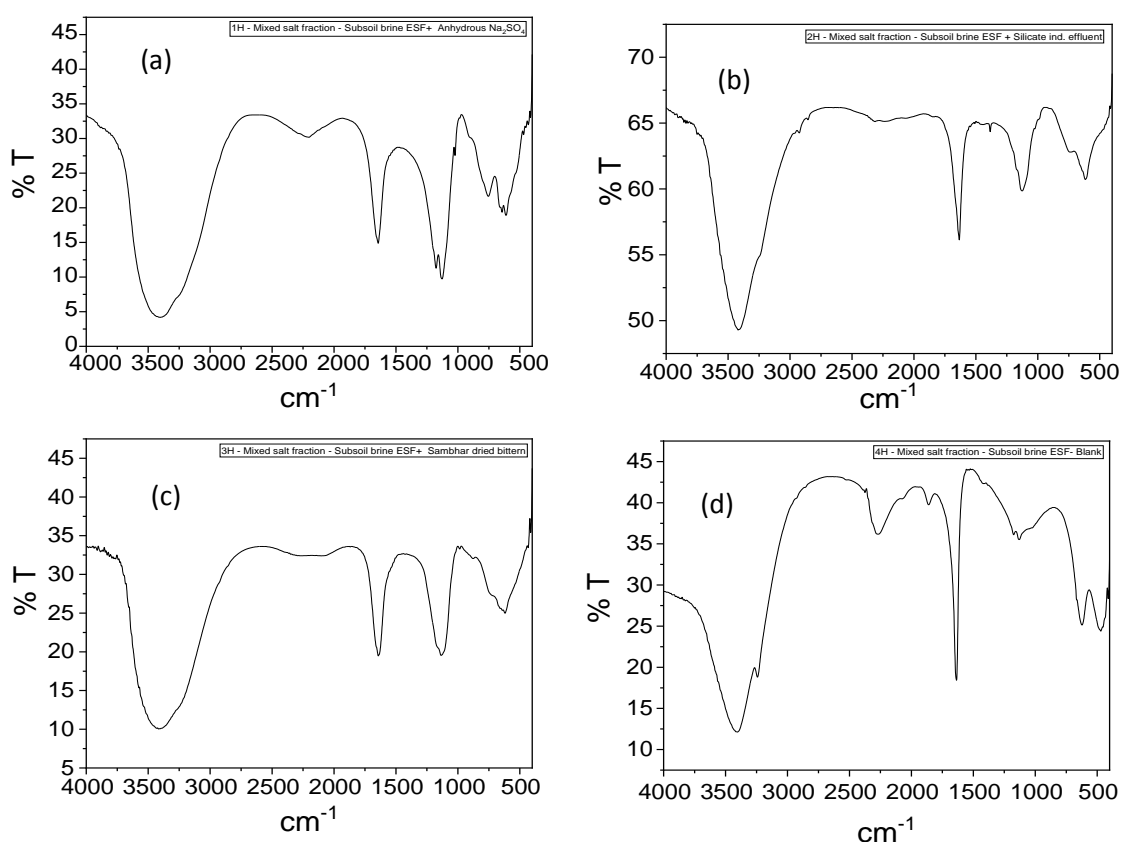


Fig 6. FTIR spectra of mixed salts precipitated from subsoil brine using different additives (a) Na_2SO_4 (anhydrous) (b) Silicate industry effluent (c) Sambhar dried bittern (d) No additive.

CONCLUSION

We have shown that industrial effluents containing sodium sulphate can be directly used in solar salt fields for improving quality and yield of salts produced from sulphate deficient sub-soil brines. Chemical and spectral analysis indicates that salts are precipitated with higher purity as compared to the salts produced from neat sub-soil brines. The crude salt obtained after crystallization of common salt can also be upgraded to industrial grade salt just by washing with appropriate amounts of fresh water. At higher densities, similar to that obtained from seawater, Kainite type double salt is obtained from effluent treated brines whereas untreated brine resulted in precipitation of Carnallite type double salt. Studies indicate that the method of addition of sodium sulphate containing effluents in sub-soil brines stoichiometric ratios can not only mitigate the environment hazards of effluent discharge but can help in improving the quality and productivity of crystallized salts in solar salt works in an economical manner.

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Conflict of interest

The authors declare that they have no conflict of interest.

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