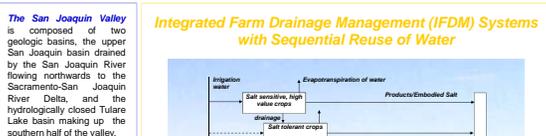
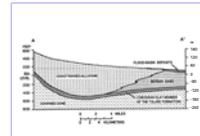


Salt Separation and Purification Concepts in Integrated Farm Drainage Management Systems

Agriculture on the west side of the San Joaquin Valley of California, like many irrigated arid land agricultures, suffers from increasing soil salinity and water logging and faces large scale land retirement in the near future if salts and subsurface drainage cannot be removed. Following discovery of avian deformities and mortalities at Kesterson reservoir due to high selenium levels, closure of drains originally intended to convey subsurface drainage water out of the Valley left farmers with few alternatives. Integrated farm drainage management (IFDM) systems employing sequential water reuse have emerged in recent years as potential phytoremediation techniques to improve salinity management. Development of acceptable final salt removal approaches is critical to the overall success of such systems. Solubility characteristics of sodium sulfate offer the potential to recover purified sulfate for commercial markets. Salt separation and purification using solar concentration and ambient cooling processes are currently being analyzed and tested. Sodium sulfate recoveries depend on the composition of the drainage feed to the concentrator along with local meteorological conditions and may range from as low as 28% to more than 85% of total salt.

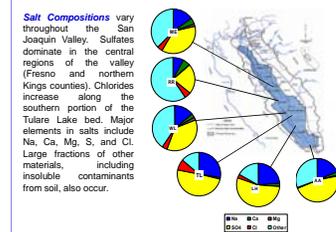


The western valley is divided into three major hydrologic zones: 1) an upper semi-confined zone to an unconfined aquifer, 2) a confining clay layer (the Corcoran clay), and 3) a confined aquifer below the clay. The upper semi-confined zone is comprised largely of three other hydrologic units including a Coast range alluvium extending from the western Coast mountain range towards the center of the valley and running over a Sierran sand deposit extending from the east. Flood basin deposits from the San Joaquin River are located in the valley trough. The Corcoran clay layer is an intrazonic zone of multiple clay layers interbedded with more permeable materials. The confined layer below is comprised principally of flood basin, deltaic, lacustrine, and alluvial deposits. The Tulare Lake basin is characterized by dry or ephemeral lakebeds and lake sediments in addition to the three hydrogeologic subunits of the semi-confined zone found throughout the valley. Marine Coast range sediments contain salts and various trace elements including selenium, boron, molybdenum, and arsenic. Irrigation dissolves these into shallow groundwater and drainage water flows. Concentrations are lower in the Sierran sediments to the east.

The western valley includes about 1 million ha of irrigable farm land. About 40% of the area is currently impacted by high water tables, drainage restrictions, and salt accumulation. In the absence of an out-of-valley drainage disposal alternative and given the adverse environmental impacts of drainage disposal in evaporation ponds and rivers, farmers and the state have attempted to identify on-farm or regional solutions for managing groundwater, drainage water, and salt. One alternative developed over the last two decades involves sequential reuse of water on crops of increasing salt tolerance. This integrated on-farm drainage management (IFDM) system has evolved from an agroforestry-based phytoremediation concept to a combined approach utilizing multiple stages of plant growth followed by a final physical salt removal step. The IFDM system has been implemented in various forms at several sites in the valley and has apparently been effective in avoiding toxic accumulations of salt in the root zones of the main production areas and in improving soil quality on previously salt affected lands. The reuse of drainage water in the system is intended to reduce the total volume of water requiring final disposal or processing. The system relies on well designed drainage systems to collect water percolating below the root zone. It is vulnerable to deep percolation and water migrating from other areas. Crop selection depends on local salinity and concentrations of boron and other elements.

Sources of salt in the western San Joaquin Valley.

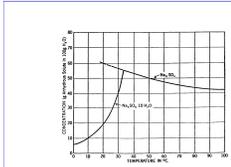
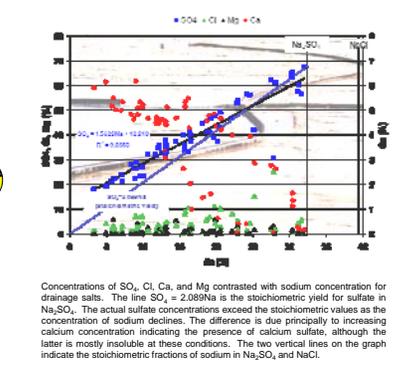
Source	Quantity of Salt (Tg yr ⁻¹)
Imported through Delta	1.80
Groundwater pumping	0.88
Local stream diversion	0.27
Lateral seepage inflow	0.14
Canal losses and precipitation	0.09
Native soil solubilization	2.56
Total	5.54



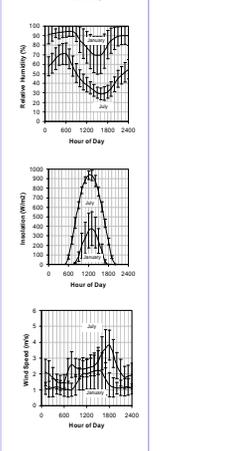
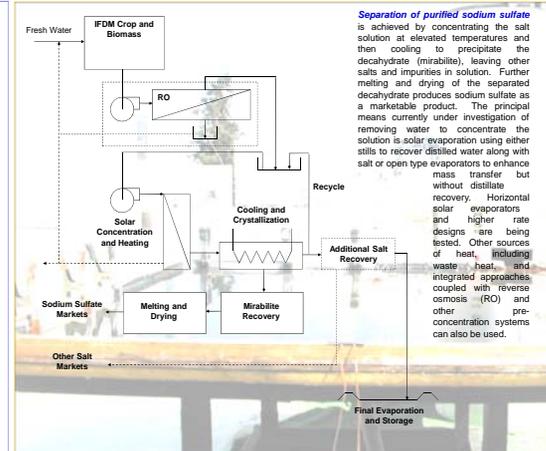
Normalized mean concentrations of salts and Na to SO₄ weight ratios*

Location	Na	Ca	Mg	Cl	SO ₄	K	NO ₃	Se	Na ₂ SO ₄
LAH	28.80	2.75	0.18	3.27	65.05	1.037	430	36	5
ARC	15.42	33.48	0.97	11.88	53.21	2.265	3,395	16,937	68
TL	31.84	0.24	1.56	9.18	57.04	1.254	129	16	1
WV	24.50	4.47	1.33	6.59	61.90	1.560	452	42	1
LA	27.62	0.29	1.13	1.28	66.76	619	670	5	0.41
ME	24.44	6.96	2.47	6.19	59.54	1.109	2,904	13	0.41
Mean	25.90	5.17	1.80	6.39	60.43	1.000	874	34.34	16

*Total = 100%. Na₂SO₄ stoichiometric ratio = 0.48.



Salt Separation and Purification
The basis for the solar salt separation process is the fractional crystallization of sodium sulfate decahydrate (Na₂SO₄·10H₂O, mirabilite or Glauber's salt) from solution using the distinctive solubility characteristic of this compound. This same fractional crystallization is standard industrial practice for the commercial production of sodium sulfate (Na₂SO₄, thenardite) from natural sources, although the industrial process typically employs substantial energy input for cooling. The decahydrate solubility increases steeply with temperature. The concentration in a pure liquid solution in equilibrium with the solid decahydrate increases from 6 g per 100 g pure water (pH₂O) at 0°C to 55 g per 100 g at 32.4°C. At the latter temperature, the decahydrate solubility becomes equal to the anhydrous sodium sulfate solubility. Whereas the decahydrate solubility increases with increasing temperature, solubility decreases with increasing temperature for solutions in equilibrium with the anhydrous solid. The anhydrous sulfate is unstable at temperatures below the transition temperature of 32.4°C and will crystallize as decahydrate if solid decahydrate is introduced (e.g. as seed crystal) or is otherwise present. The rejection of other ions during sodium sulfate crystallization is high, so good purity can generally be obtained in mixed salt systems.



Sodium sulfate recovery can reduce the total quantity of residual salt needing final storage. Concentrations and masses were predicted for concentrate following solar evaporation, residual solution following precipitation of sodium sulfate, and residual salt evaporite following final evaporation of water for given influent concentrations. Sulfate is assumed to crystallize as pure mirabilite (composition given for thenardite form). In practice Mg, Cl, and other elements including Se are also present in varying amounts. Mass quantities for the RR site data are computed on the basis of actual salt concentrations and water flows.

Principal components and salt masses, RR site data

Component	Unit	Concentration	Mass	Recovery
Na ₂ SO ₄	kg	1,200	1,200	1,200
Ca	kg	100	100	100
Mg	kg	100	100	100
Cl	kg	100	100	100
Se	kg	100	100	100

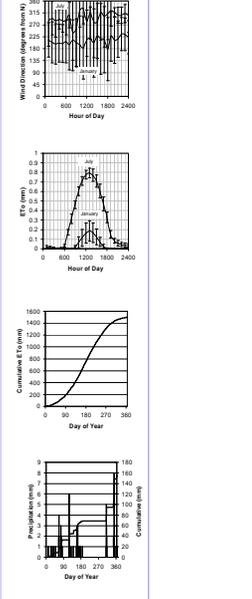
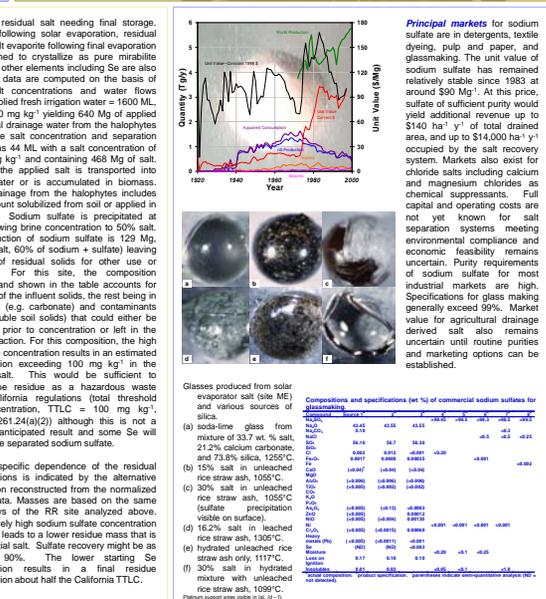
Annual applied fresh irrigation water = 1600 ML
TDS = 400 mg kg⁻¹ yielding 640 Mg of applied salt. Total drainage water from the halophytes feeding the salt concentration and separation system was 44 ML with a salt concentration of 10,620 mg kg⁻¹ and containing 468 Mg of salt. Some of the applied salt is transported into ground water or is accumulated in biomass. Salt in drainage from the halophytes includes some amount solubilized from soil or applied in fertilizers. Sodium sulfate is precipitated at 15°C following brine concentration to 50% salt. The production of sodium sulfate is 129 Mg, (28% of salt, 60% of sodium + sulfate) leaving 339 Mg of residual solids for other use or disposal. For this site, the composition analyzed and shown in the table accounts for only 15% of the influent solids, the rest being in other ions (e.g. carbonate) and contaminants (e.g. insoluble soil solids) that could either be separated prior to concentration or left in the residual fraction. For this composition, the high influent Se concentration results in an estimated concentration exceeding 100 mg kg⁻¹ in the residual salt. This would be sufficient to classify the residue as a hazardous waste under California regulations (total threshold limit concentration, TILC = 100 mg kg⁻¹; 22CCR66261.24(a)(2)) although this is not a generally anticipated result and some Se will occur in the separated sodium sulfate.

Site specific dependence of the residual concentrations is indicated by the alternative composition reconstructed from the normalized AA site data. Masses are based on the same water flows of the RR site analyzed above.

The relatively high sodium sulfate concentration at the site leads to a lower residue mass at 15% of initial salt. Sulfate recovery might be as high as 90%. The lower starting Se concentration results in a final residue mass with unclassified rice straw salt, 1055°C.

Compositional and specifications (wt % of commercial sodium sulfates for glassmaking)

Material	Na ₂ SO ₄	Ca	Mg	Cl	Se
AA	95.0	0.5	0.5	0.5	0.5
RR	95.0	0.5	0.5	0.5	0.5
AA	95.0	0.5	0.5	0.5	0.5



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