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Mineral Separation and Recycle in a Controlled Ecological Life Support System (CELSS)

E. Vernon Ballou

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ABSTRACT

This report explores the background of the mineral nutrition needs of plants, considers in some detail the applicability of mineral control and separation to a controlled ecological life suport system (CELSS), and delineates steps that should be taken in a program to analytically define and experimentally test key mineral control concepts in the nutritional and waste processing loops of a CELSS.

An introductory survey is made of the mineral requirements of plants, the evidence for toxicity to plant growth by a variety of elements and ionic species, and the range of concentrations between beneficial and toxic effects. Potential problem elements or inorganic species are identified, and a brief discussion is given of salt tolerance in plants. The concept of sodium separation by accumulation in plants is considered. The impact and need for mineral separation and control in an ecological system requiring optimum plant growth and productivity is discussed.

In order to be more specific and quantitative about mineral separation needs in a CELSS, data for plant growth in a previous manned system test (Bios-3) and several calculated scenarios, along with hydroponic growth recommendations, is tabulated. Using published data as guidelines for the masses, areas, and volumes needed for higher plant production, a comparison is then made of phytotron utilizations calculated for one man day total nutrition. Finally, the results of scenario calculations are presented for 10 man, 10 year missions with various combinations of phytotron support and mineral recycle. Estimates are made of the masses of material needed to meet human nutritional requirements in the various scenarios, and it appears that mineral recycle is a favorable mode of operation. It must be emphasized, however, that the data presentation and the scenario mass calculations presented here are preliminary rather than definitive. They are designed to give an overview of the problem which would then allow a more comprehensive study of background data applied to waste product recycle and nutritional demands in a CELSS.

Potential mineral separation methods discussed in current literature are then briefly reviewed, including chromatography, fractional crystallization, flotation, membrane separations, cyclic separation processes, and non-chromatographic ion-exchange processes. From reports in the literature, it appears that each of these methods, at least, should be considered and analyzed for application to a CELSS mineral control and recycle system.

I. INTRODUCTION

This is a report on the mineral control and mineral separation problems relevant to a controlled ecological life support system (CELSS). For purposes of this report, a CELSS is defined as a concept for a proposed closed ecological life support system which will be used in spacecraft to take man on space missions in which he will provide for his own nourishment and survival by recycling waste products and producing edible products.

A major consideration necessary for the operation of a CELSS is likely to be the control of the organisms that produce food for the unit. Whether these are plants, algae, bacteria, or some organism, such as yeast, that uses products from "artificial photosynthesis", control of their growth and metabolism will be an important factor in order to minimize the size of the storage reservoirs and to maintain a stable "instantaneous" concentration of carbon dioxide and oxygen in the atmosphere. Control of growing biological entities requires that their internal control systems be affected in known ways by exposure to external conditions: gases, temperature, light, mineral concentrations in nutrient solutions, and biologically produced organic compounds in the gas and liquid phases.

Minerals in the nutrient solution are major control parameters for metabolic growth and the healthy physiological state of plants. It is vital, therefore, that the concentrations of minerals to which organisms are exposed be known and controlled at levels that are appropriate to the conditions chosen in any control scenario. Mineral separation is, therefore, an essential part of a system that will control the growth of organisms in an isolated environment, such as a CELSS.

A. Required Elements

Although the bulk of plant material, including the edible portions, comes from carbon, oxygen, and hydrogen in atmospheric gases and water vapor, and from liquid water with dissolved gases, there are a number of other elements, generally in the form of inorganic minerals and soluble salts, which must be provided in minimum amounts for proper growth of plants. The generally accepted list of essential nutrients includes 13 elements, of which 6 (N, K, Ca, Mg, P, and S) are termed "macro nutrients" and 7 (Cl, B, Fe, Mn, Zn, Cu, and Mo) are termed "micro nutrients" (1-7). The 13 elements of the essential nutrient list are those that meet three criteria for all higher plants, namely (1) the plant cannot complete a life cycle without it, (2) the element cannot be substituted by another element, and (3) the element becomes a constituent of an essential metabolite or enzyme in the plant.

The list of 13 is a simplification of the total picture of mineral nutrition for higher plants. A host of other elements may (a) be essential to some species of higher plants, (b) improve plant growth, or (c) be capable of partial substitution for an essential element. Elements in these categories are Na, which is essential to some halophytes (2,3,7), Co, which is essential for legumes (2,3,5,6), Se and Si, which are accumulated by some species and may be required by some (2,6), and V and I, which are required by or important to some species (2,5,6,7). Other elements which are functional or beneficial to various higher plant species include Li, Rb, Cs, Be, Al, Ba, Ga, Sb, As, Cd, Ce, Cr, Nb, F, La, Pb, Hg, Ni, Sc, Sr, Tl, Th, Sn, Ti, U, and Zr (6,8).

When algae, fungi (yeast), and bacteria are included for consideration in a food or atmospheric control recycle loop, the elemental needs remain similar, but not identical, to those for the higher plants. Table I compares elemental requirements in a qualitative manner. For algae, Ca becomes a micronutrient (2) and, in some algae, Rb may be substituted for K and Sr for Ca (2). Cl is often a macronutrient, and Br can sometimes substitute for Cl in algae (2). K and Ca become micronutrients for fungi (2), Rb can substitute for K in some bacteria (2), while Ca, when required, is a micronutrient (2). Co is required for N fixing bacteria.

B. Toxic Elements

The elements that can have toxic effects on plants include many of the same elements that are essential or beneficial in lower concentrations or different ionic forms. A list of elements known to have toxic effects under some conditions, with referenced comments, is given in Table II. In a recent study of toxicity (10), it was found that all ions studied caused lethal toxicity in the sub and low meq/liter range. The ions studied, in order from most toxic to least toxic were Cd^{++}, VO_3^-, Co^{++}, Cu^{++}, Ni^{++}, CrO_4^{--}, Zn^{++}, and Mn^{++}. In the case of Zn^{++}, Cu^{++}, and Mn^{++}, the required concentration for nutrition was 1% of the toxicity threshold.

When irrigation is carried out with recycled domestic waste water effluent, 5 elements, B, Cl, Cu, Ni, and Zn could be present in amounts potentially toxic, and should be monitored (10). It is recommended (11) that, for continuous use as irrigation water, effluent should contain no more than 0.005 ppm Cd, 0.2 ppm Cu, 0.5 ppm Ni, or 5.0 ppm Zn. However, the concentration that has been recommended for continuous use in irrigation water will be too high when there is no soil present (soilless culture) to ameliorate the toxicity (12).

Heavy metal toxicity has been noted as producing

TABLE I

Essentiality of Mineral Elements for Plants *

Mineral	Higher Plants	Algae	Fungi	Bacteria
N	+	+	+	+
K	+	(+)	+	(+)
Ca	+	+	(+/-)	(+/-)
Mg	+	(+)	+	+
P	+	+	+	+
S	+	+	+	+
Cl	+	+	-	(+/-)
B	+	(+/-)	-	-
Fe	+	+	+	+
Mn	+	+	+	+
Zn	+	+	+	(+/-)
Cu	+	+	+	(+/-)
Mo	+	+	+	(+/-)
Na	(+/-)	(+/-)	-	(+/-)
Co	-	(+/-)	-	(+/-)
Se	(+/-)	-	-	-
Si	(+/-)	(+/-)	-	-
V	-	(+/-)	-	-
I	-	(+/-)	-	-

\+ = essential
\- = not known to be essential
(+/-) = essential for some, but not generally
(+) = generally essential, but can be substituted in some

* adapted from ref. (2), p. 62

TABLE II

Elements Known to Have Toxic Effects on Plants

Element	Comment	Reference
Na	often inhibits growth	2
Li	often inhibits growth	2
Pb	toxic	2
	toxic	9
Zn	toxic	2
	toxic at higher levels	4
	never exceed 1 ppm	6
Cu	>1 ppm toxic	7
	toxic	2
	fungicide, higher plant toxicity varies, lettuce sensitive	4
	>1 ppm toxic	6
N	excess NH4+ toxic	4
P	excess causes Fe deficiency	4
K	excess toxic	4
Mg	excess toxic	4
S	large excess toxic	4
Ca	excess toxic	4
B	>1 ppm toxic	7
	a few ppm range between deficiency and toxicity	4
	1.1 ppm optimum, >5 ppm toxic	6
Mn	toxic at higher levels (>10 ppm for lettuce)	4
	toxic at 1-80 ppm, Fe/Mn ratio must be controlled	6
HCO3-	high levels toxic	4
Cl-	only micronutrient that is without ill effect at relatively high concentration	7
	excess toxic	4
I	>1 ppm toxic	6
Al	>1 ppm toxic	6
	toxic	9
Fe	don't exceed 5 ppm in fertilizer, toxic at high concentration	6
Se	excess toxic to plants, but 1/12 Se/S allows 18 ppm Se, 5 ppm stimulates plants but 1 ppm toxic to animals	6
Co	>0.1 ppm toxic	6
Ni	>1.5 ppm toxic	6
Pd	toxic at low concentration	6
Ag	toxic	9
	>2 ppm toxic	6
Sr	toxic in absence of Ca	6
Hg	toxic	9
W	toxic	9
Ge	toxic	9

chlorosis in mustard plants, where the order of toxicity, from greatest to least, was Cu > Ni > Co > Zn > Cr > Mn (13). In these tests 2 ppm of each metal was added to the nutrient solution. The plants were harvested in 21 days and the average fresh weights were 0.58, 0.69, 0,73, 1.29, 3.26, and 3.83, respectively, for plants grown in solutions containing the metals listed previously, at the 2 ppm level. In contrast, the average fresh weight of the plants was 5 g when none of the above heavy metals were added to the nutrient solution

C. Salt Tolerance

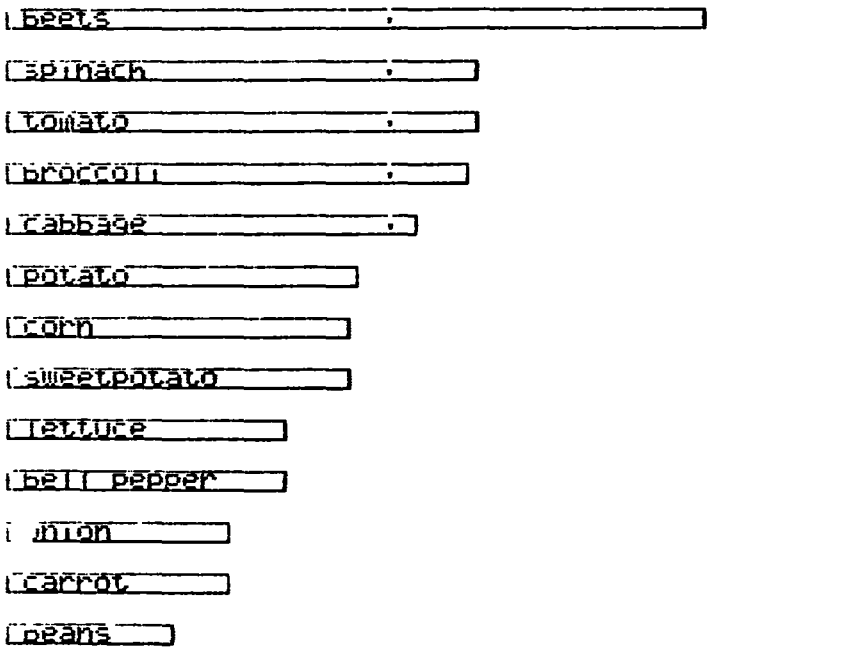
The salt tolerance of higher plants is a problem that is separate from, but related to, toxicity and nutritional requirements. This is because there are a variety of salts that do not have a specific toxicity effect at low concentration levels, but may be toxic at higher concentration levels, or inhibit growth by (a) raising the osmotic pressure of the nutrient solution, and (b) reducing uptake of essential elements to below that required for optimum growth. The salt of chief concern is usually NaCl, because it is more often present in high concentration than other salts of this type. A quantitative estimate of the effect of salinity (as expressed by the specific electrical conductivity of the nutrient solution) is given in Fig. 1, which is taken from a figure in (14) which cites data in (15).

The other side of the picture for higher plant growth is that some plants, known as halophytes, grow well in high salt concentrations in the nutrient solution; and some of these species, the obligate halophytes, require NaCl for their growth. In addition, a number of species of plants not known to be halophytes, can be genetically selected to survive and grow in high salt concentrations, although generally not as productively as in low salt concentrations.

Although the development of salt resistant genetic species may be applicable soon to some crops in irrigated high- saline environments, it does not appear that the technology is at a stage of development where a balanced diet could be grown in a closed system, such as a CELSS, without regard for the salt concentration in the nutrient solution. This is because the known halophyte plants are, generally, not edible and the work on genetic breeding of other species for salt tolerance has been very limited to date. The yields of salt tolerant genetic species in sea water irrigation experiments has not equalled those of comparable plants grown in low salt environments (16). One author (2) noted that we can breed salt tolerance into crop species or usefulness into salt-tolerant wild plants,but "neither of these strategies has been tried in any sustained, energetic manner".

Figure 1

SALT TOLERANCE OF VEGETABLE CROPS *
(50% yield reduction)



* from (14) and (15)

In a more quantitative assessment of salt tolerance, it has been pointed out (4) that waters with less than 500-700 ppm total salts, and with Na+ concentration in the 200-400 ppm range and Cl- concentration in the 300-600 ppm range, may be used "without taking any special measures" for nutrient solutions. Waters with total salt in the 700-3000 ppm concentration range, or those up to 700 ppm whose Na+ and Cl- content are higher than the preceeding figures, may be used if precautions are taken in making up the nutrient solution (4). Waters with total salt over 3000 ppm or whose Na+ concentration is 0.1-1.0% and Cl- concentration is 0.2-1.0% "should generally not be used unless proven suitable by experiment" (4). These figures apply to commercial hydroponic higher plant growth using local water, including that from arid regions; and are not necessarily a guide to optimum plant growth in closed ecological systems.

The crops that can be grown in saline water may be divided into groups that are tolerant to salt (8-12 mmho/cm specific conductivity = 5000-7700 ppm *), moderately tolerant to salt (4-8 mmhos/cm specific conductivity = 2600-5000 ppm), and sensitive to salt (2-3 mmhos/cm specific conductivity = 1300-1900 ppm). A maximum salt concentration in hydroponic nutrient solution of 1920 ppm * for tomatoes and 1600 ppm * for cucumbers has been recommended (17). (* Note - conversion from specific conductivity to ppm using conversion factor in (4), p. 108.)

However, saline tolerance also depends on the plant growth stage, with younger plants usually more sensitive to salt than more mature plants (4). Yields for mature plants, however, may be 10-25% lower in saline conditions (4). "Since salinity leads to stunted growth and a decrease in leaf, bud, and root development, the number and quality of vegetables, fruits, and flowers are affected and the percentage of first grade crop is reduced" (4). "Direct toxicity due to sodium and chloride ions of saline water is common, especially in stone fruits, grapes, strawberries, roses, etc. These toxic effects occur below the osmotic levels restricting yields in these crops" (4). Table III shows tolerance levels to NaCl by different plants, ranging from 370 to 2630 ppm. Ranges of similar magnitude are given for tolerance of MgSO4, MgCl2, Na2CO3, Na2SO4, and NaHCO3 (18). According to the same author, "there is no doubt that salinity adversely affects the growth of plants." Numerous experiments show that the detrimental effects are already evident during germination. Under saline conditions, germination is strongly retarded, the growth processes of plants are inhibited, and dwarfed plants result" (18).

Possibly the most successful growths of a species of higher plant suitable for food in a high saline nutrient solution are the Bodega Bay (CA) experiments on barley irrigated with sea water (19). The barley was bred from a large gene pool for saline water resistance. Yields up to

TABLE III

Maximum Concentration of NaCl Tolerated without Toxic Symptoms for Different Plants

Plant Species	Normality (N) *	ppm **
wheat	0.045	2630
maize	0.040	2340
sorghum	0.015	880
oats	0.020	1170
cotton	0.00625	370
sugar beet	0.025	1460

* N values from ref. (18), p. 34 - Table 9,
** ppm calculated from normality

75% of the world average for barley have been noted (16). Although these exerimental results appear attractive, they represent a limited application of high salinity culture under favorable conditions. High NaCl concentration is often very bad for plant productivity, although some plants tolerate it more than others (20).

D. Minimum and Maximum Elemental Concentration

A large variety of elements that exist as ionic species in nutrient solution are essential or helpful to plant growth at certain concentrations. In addition, a large variety of elements as ionic species are inhibitory, or toxic, at other concentrations. A number of elements exist in both classes. It would seem that a concentration range could be established for each element or ionic species; and that the mineral control system in a CELSS would then function, with input from an analytical system, to keep all concentrations in an appropriate range and, preferably, at the optimum concentration for the food production cycle.

The actual specification of a concentration range for each ionic species is not so straightforward. For one consideration, the minimum, maximum, and optimum concentration of an ionic species in the nutrient solution often varies between higher plant species (and, no doubt, is different for algae, fungi, and bacteria) and for different genetic breeds of the same species and for the stage of plant development. The concentrations of different ions are often interactive in their nutritional or toxic effects, so that a change in concentration of one ionic type should be balanced by changes in the concentrations of other ions.

The available data on nutrient solution concentration is usually that recommended for various compositions of nutrient solutions (Table IV) assuring adequate supplies of essential elements for most higher plants (1,2,3,4). It is generally assumed that any depletion or excess can be rectified, if necessary, by discarding the nutrient solution and/or adding fresh nutrients (1).

Recommended minimum and maximum concentrations to be found absorbed in plant tissue are available for some elements (Table V). These concentration in the plant are, however, not simply related to nutrient solution concentrations. Factors such as root spacing and solution flow rate affect the nutrient absorption. It has been shown that nutrient solution in a single pass flow through a hydroponic bed can have adequate minimum amounts of essential elements at levels considerably lower than those usually recommended for hydroponic growth (21). It has been found that, as a first approximation, either a Freundlich or Langmuir isotherm is applicable to the relation between external ion concentration and ionic species absorption (7). However, departure from the hyperbolic relationship occurs

TABLE IV - PART 1

Composition of Nutrient Solutions, ppm

Originator:	Resh-A	Resh-B	Resh-C	Hoagland	Hoagland and Arnon	Schwarz	Schwarz
Date:	1971	1971	1971	1919	1938	-	1975
Reference:	1	1	1	1	1	1	4
Recommended for:	tomato seed-lings	14-24" tomato plants	>24" tomato plants	-	-	-	-
Ca++:	98.5	148	197	200	160	124	124
Mg++:	22	33	44	99	48	43	43
Na+:	-	-	-	12	-	-	-
K+:	200	300	400	284	234	312	312
N as NH4+:	10	20	30	-	14	-	-
N as NO3-:	80	110	145	158	196	-	-
Total N:	90	130	175	158	210	128	168
P as PO4---:	40	55	65	44	31	93	93
S as SO4—	83.2	144.3	197.5	125	64	160	480
Cl-:	-	-	-	18	-	-	-
Fe:	2	2	2	as req.	0.6	-	-
Mn:	0.5	0.5	0.5	-	0.5	-	-
Cu:	0.03	0.03	0.03	-	0.02	-	-
Zn:	0.05	0.05	0.05	-	0.05	-	-
B:	0.5	0.5	0.5	-	0.5	-	-
Mo:	0.02	0.02	0.02	-	0.01	-	-

TABLE IV - PART 2

Composition of Nutrient Solutions, ppm

Originator:	C.M.Johnson (modified)	Berry	H.JohnsonJr.	California	California
Date:	1957	1978	1980	-	-
Reference:	2	3	17	1	4
Recommended for:	many species	tomatoes and cucumbers	-	-	-
			-	-	-
Ca++:	160	100	83	160	160
Mg++:	24	24	24	48	48
Na+:	-	11	-	-	-
K+:	235	140	140	234	234
N as NH4+:	-	105	103	15	-
N as NO3-:	-	-	-	196	-
Total N:	224	105	103	211	210
P as PO4---:	62 (H2PO4-)	31 (H2PO4-)	33 (H2PO4-)	31	31
S as SO4--:	32	32	32	64	192
Cl-:	1.77	18	-	-	-
Fe:	1.12	2.5	2.5	-	-
Mn:	0.11	0.25	0.25	-	-
Cu:	0.032	0.01	0.01	-	-
Zn:	0.131	0.025	-	-	-
B:	0.27	0.25	0.25	-	-
Mo:	0.05	0.005 (MoO4)	0.005	-	-

TABLE IV - PART 3

Composition of Nutrient Solutions, ppm

Originator:	Purdue	New Jersey	South Africa	Douglas	
Date:	-	-	-	1976	
Reference:	4	4	4	6	
Recommended for:	-	-	-	-	
				Limits	Average
Ca++:	180	180	320	300-500	400
Mg++:	24	55	50	50-100	75
Na+:	-	-	-	-	-
K+:	390	90	300	100-400	250
N as NH4+:	-	-	-	-	-
N as NO3-:	-	-	-	-	-
Total N:	98	145	200	150-1000	300
P as PO4---:	31	71	65	50-100	80
S as SO4--:	576	288	-	200-1000	400
Cl-:	-	-	-	-	-
Fe:	-	-	-	2-10	5
Mn:	-	-	-	0.5-5	2
Cu:	-	-	-	0.1-0.5	0.5
Zn:	-	-	-	0.5-1	0.5
B:	-	-	-	0.5-5	1
Mo:	-	-	-	0.001-0.002	0.005

TABLE V

Literature Recommendations for the Concentration of Elements Desirable in Dried Plant Tissue

	Range Found in Apparently Healthy Plants, ppm (17)		Internal Concentrations Considered Adequate (1,2)	
Element	Tomatoes	Cucumbers	Elemental form	ppm
N as NO3	14,000-20,000	10,000-20,000	NO3-,NH4+	15,000
P as PO4	6,000-8,000	8,000-10,000	H2PO4-, HPO4--	2,000
K	50,000-80,000	80,000 150,000	K+	10,000
Ca	20,000-30,000	10,000 30,000	Ca++	5,000
Mg	4,000-10,000	3,000 7,000	Mg++	2,000
Fe	40-100	90-120	Fe++,Fe+++	100
Zn	15-25	40-50	Zn++	20
Cu	4-6	5-10	Cu+,Cu++	6
Mn	25-50	50-150	Mn++	50
Mo	1-3	1-3	MoO4--	0.1
B	20-60	40-60	BO3---, B4O7-	20
S			SO4--	1,000
Cl			Cl-	100

if (a) the absorption sites become saturated and uptake depends on the synthesis of unoccupied binding sites, (b) diffusion is a limiting factor in transport of ions to the binding sites, (c) a fraction of the salt absorbed is taken up passively by mass flow (7). Thus, it appears possible, if sufficient data were available, to calculate and predict the solution concentration to bring about the necessary or optimum tissue concentration of elements in any plant species. However, it is unlikely that data on the relationship between solution concentration and amount absorbed is available for the mixtures of ions at various concentrations in solution and the number of plants in various stages of growth to be expected in a CELSS. Therefore, empirical correlations, together with observations of solution concentrations, plant tissue elemental concentrations, and plant development characteristics, should be useful in determining the operation of the mineral control system for a CELSS.

E. Identification of Problem Elements

Although the identification of problem elements - or problem minerals or ionic species - could be a significant task in a research program, some guidelines and a preliminary identification will be stated here. One might expect any of the following factors to lead to special problems for a CELSS mineral control system:

(1) a narrow range could exist between the concentration at which a mineral nutrient is essential or beneficial to plant development and the concentration at which it is detrimental or toxic to plant development,

(2) the presence of any species with a low or very low toxicity threshold and which might deliberately or inadvertently be present in a solution which was part of the plant or human nutrition intake,

(3) the case in which a specific ionic form is needed for optimal nutritional input of an element and the element appears after recycle processing in a form or forms that are not useful or desirable as nutrients,

(4) an element could be present which substantially interferes with the uptake of another, and possibly essential, element for plant nutrition - a form of toxic action even though the element is not specifically toxic,

(5) an element could be present which accumulates in the edible portions of plants at levels which are not toxic to the plants but are toxic to humans,

(6) an element or mineral species could be present for which special processes must be undertaken (possibly requiring special reagents or equipment in addition to that used for control of the majority of elements whose concentrations are controlled by the mineral control system),

(7) an element or mineral could be present whose concentration built up in the plant nutrient solution to a level which could inhibit plant development by increasing

the osmotic pressure of the solution.

In Table VI, a compilation is made of reported beneficial and toxic concentrations of elements in a plant nutrient solution. Table VII gives an estimated control range for each element, together with an estimate of whether control will be needed, and whether it will be a problem. The check list of elements which will need to be controlled leaves out those which do not appear likely to be present as materials of construction or of use in living arrangements and scientific and industrial experiments in a CELSS. However, a great variety of elements are ubiquitous in all materials involved in human activities and it would be an unacceptable risk to fail to consider, at least, removal methods for elements which are not clearly anticipated, but are harmful to plant or animal metabolism.

In an effort to further identify which elements would be allowed in a potential manned spacecraft for a CELSS, contact was made with the Materials Technology Branch and the Metallic Materials Section of the Structures and Mechanics Division, Directorate of Engineering and Development, NASA Lyndon B. Johnson Space Center, Houston, TX. It was ascertained that there is no general list of materials that are allowed in the construction of a manned spacecraft (24). However, there is a Selection List of Materials for Shuttle (JSC-09604). This list has been obtained, and could be a guideline for elements that might enter the mineral nutrient solution through corrosion, or other processes in the vehicle recycle loop. The list is, however, only applicable to prospective Shuttle flights, and a new list would be made up for any space station or prospective CELSS type mission (24).

Elements are identified as potential control problems (Table VII) for a variety of reasons (see Table VI for toxic concentrations and references). NH_4^+ is a plant nutrient, but toxic at higher concentrations. NO_2^- also has a reported toxic effect. These species are listed as potential problems because they may be in appreciable concentrations in the effluent of a waste oxidation subsystem, and there may have to be a means of conversion to NO_3^- to assure optimum plant growth with N recycle. Cu, B, Zn, and Mn are all essential micronutrients for higher plants, but are toxic to plant development at low concentrations (although Mn is tolerated at higher concentrations than the others). Therefore, they have to be controlled in the plant nutrient solution within narrow limits.

I and Al may be present in a CELSS (I is essential for the human thyroid gland and Al is present in many alloys) They are apparently not essential, but beneficial, in low concentrations in the mineral nutrient solution, but toxic at slightly higher concentrations. As, Ba, Be, Hg, Pb, and Cd may also be present, even if unwanted, and are toxic to

TABLE VI - PART 1

Reported Minimum Concentrations for Beneficial Effects and Minimum Concentrations Showing Toxic Effects to Plant Growth for Various Elements

Element	Elemental form	Minimum Adequate or Beneficial concentration, ppm	Minimum Toxic concentration, ppm	Reference
N	-	~300	-	6
	NO_3^-	6	-	22
	NO_3^-	-	no problem	4
	NO_2^-	-	toxic effect	4
	NH_4^+	-	excess toxic	6,4
	NH_4^+	0.8	1.2	22
Ca	-	300	500	6
Mg	-	50	100+	6
P	-	50	100+	6
			excess = Fe deficiency	4
K	-	100-400	-	6
S	-	200-1000	-	6
			very large excess toxic	4
Cl	-	5	-	6
		10-20	O.K.	4
			O.K. at relatively high conc.	7
Cu	-	0.5 optimum	1.0	6
	-	0.05	1.0	7
	Cu^{++}	0.002	0.48	10
I	-	0.01	1.0	6
Al	-	1.0	10	6
B	-	1.1 optimum ***	0.5 **	6
	BO_3^-	0.41	-	10
	-	0.05	1.0	7
Fe	-	5 or less	-	6
Mn	-	0.003-5	1-80	6
	-	-	10 ***	4
	Mn^{++}	0.05	88	
Mo	-	0.001	-	6
	-	0.0016	-	10
Se	-	5	0.1-18 *****	6

* tomatoes, ** citrus, *** overlap of beneficial and toxic for different species
**** lettuce, ***** 1 ppm toxic to humans

TABLE VI - PART 2

Reported Minimum Concentrations for Beneficial Effects and Minimum Concentrations Showing Toxic Effects to Plant Growth for Various Elements

Element	Elemental form	Minimum Beneficial concentration, ppm	Minimum Toxic concentration, ppm	Reference
Zn	-	0.1-0.2	1.0	6
	Zn^{++}	~0.005	2.1	10
	-	-	2	13
Sb	-	some	-	6
As	-	low	low	6
Ba	-	small amount	depends on Ca	6
Be	-	small amount	- *	6
Bi	-	minute	-	6
Br	-	very low	-	6
Cd	-	unknown	-	6
	Cd^{++}	-	0.09	10
Ce	-	unknown	-	6
Cs	-	small	-	6
Cr	-	not understood	-	6
	CrO_4^{--}	-	1.1	10
	-	-	2	13
	CrO_4^{--}	-	1.1	23
Co	-	0	0.1	6
	Co^{++}	-	0.38	10
	-	-	2	13
	Co^{++}	-	0.6	23
Nb	-	inconclusive	-	6
F	-	traces	traces	6
Ca	-	essential to some (conc. not given)	-	6
La	-	addition beneficial (conc. not given)	-	6
Pb	-	-	low concentration	6

* toxic to humans

TABLE VI - PART 3

Reported Minimum Concentrations for Beneficial Effects and Minimum Concentrations Showing Toxic Effects to Plant Growth for Various Elements

Element	Elemental form	Minimum Beneficial concentration, ppm	Minimum Toxic concentration, ppm	Reference
Li	-	stimulating (conc. not given)	-	6
Hg	-	no information available	-	6
Ni	-	small amounts	1.5	6
	Ni^{++}	-	0.56	10
	-	-	2	13
Pd	-	-	low concentration	6
Rb	-	no effect	no effect	6
Sc	-	may be essential (no conc. given)	-	6
Ag	-	-	0.2	6
	Ag^{+}	-	1.0	23
Sr	-	small amount in presence Ca	small amount in absence Ca	6
Tl	-	below 0.1	1.0	6
Th	-	unknown	-	6
Sn	-	unknown	-	6
Ti	-	up to 5 ppm	-	6
	Ti^{+++}	-	5	23
W	-	unknown	-	6
V	-	extremely small	appreciable concentration	6
	VO_3^-	-	0.41	7
	VO_3^-	-	10	
Y	-	unknown	-	6
Zr	-	unknown	unknown	6
Na	-	-	370-2630	18
	-	-	1000	12
	-	-	200-400	4
	-	-	50	1

TABLE VII - PART 1

Estimated Control Ranges for Mineral Nutrients in a CELSS

Element	Elemental form	Estimate control needed	Estmate potential control problem	Concentration range to maintain in nutrient solution, ppm
N	NO_2^-	*	*	max. unknown
	NO_3^-	*		> 300
	NH_4^+	*	*	< 1
Ca	Ca^{++}	*		300-500
Mg	Mg^{++}	*		50-100
P	PO_4^{---}, $H_2PO_4^-$	*		50-max. unknown
K	K^+	*		100-max. unknown
S	SO_4^{--}	*		> 200
Cl	Cl^-	*		> 5
Cu	Cu^{++}	*	*	0.05-1.0
I	I^-	*	*	0.01-1.0
Al	-	*	*	1.0-10
B	-	*	*	0.05-.50
Fe	-	*		> 5
Mn	Mn^{++}	*	*	0.05-10
Mo	-	*		> 0.001
Se	-	*	*	< 0.1
Zn	Zn^{++}	*	*	0.1-1.0
Sb	-			< max. unknown
As	-	*	*	< max. unknown
Ba	Ba^{++}			min. and max. unknown
Be	-	*	*	< max. unknown
Bi	Bi^{+++}			max. unknown
Br	Br^-			max. unknown
Cd	Cd^{++}	*	*	< 0.09
Ce	-			max. unknown

TABLE VII - PART 2

Estimated Control Ranges for Mineral Nutrients in a CELSS

Element	Elemental form	Estimate control needed	Estmate potential control problem	Concentration range to maintain in nutrient solution, ppm
Cs	Cs+			< max. unknown
Cr	Cr+++, CrO4-	*	*	< 1.0
Co	-	*	*	< 0.1
Nb	-			max. unknown
F	F-	*	*	< max. unknown
Ga	-			max. unknown
La	-			max. unknown
Pb	Pb++	*	*	< max. unknown
Li	Li+			max. unknown
Hg	Hg+, Hg++	*	*	< max. unknown
Ni	Ni++	*	*	< 0.5
Pd	-			max. unknown
Rb	Rb+			max. unknown
Sc	-			max. unknown
Ag	Ag+	*	*	< 0.2
Sr	Sr++	*		< max. unknown
Tl	-			< 1.0
Th	-			max. unknown
Sn	-			< max. unknown
Ti	-	*	*	< 5
W	-			< max. unknown
U	-			max. unknown
V	-	*	*	< 0.4
Y	-			max. unknown
Zr	-	*	*	< max. unknown
Na	Na+	*	*	< 50

humans and plants. Cr, Co, Zr, Ti, W, Sn, Ag, and Ni can arise from materials degradation and corrosion and are potentially toxic to plants, although no quantitative data was found for Zr, W, and Sn. F would possibly be present in a human habitat (e.g. for protection from caries), and is toxic to plants at trace levels. Na is possibly the major problem of a CELSS mineral control system, due to its abundant presence in human diet and human waste. It can be tolerated in mineral solutions for plants at relatively high levels, but must be controlled or its build-up can greatly reduce phytotron productivity.

F. Sodium Accumulation by Plants

It has been suggested (25) that a food production scheme that concentrates sodium from very dilute solutions would be one way of dealing with recycling this element. This interesting concept leads to a consideration of halophytes. Plants which grow in saline habitat all possess special adaptations and are collectively called "halophytes". The term does not, however, refer to particular botanical taxa (2). Unlike salt-sensitive plants, halophytes are able to tolerate the high concentration of mineral ion that accumulates in their tissues (2). In addition to the toleration of high intercellular concentrations of ions, some halophytes have salt glands in their leaves which excrete salt onto the leaf surface, from which it is eventually removed by the action of wind or water (2). One species of halophyte with salt glands has been described as having 700 glands/mm2 of leaf surface, which may excrete up to 1 ml of liquid per hour, containing 0.05 mg NaCl (7). The amount of NaCl is considerable, but the concentration of 0.05 mg/ml (0.05 g/L or 50 ppm) is far lower than that of most saline waters. It has also been reported that, under optimum conditions, the concentration of salt in the excreted fluid is higher than the mean salt concentration of the leaf tissue (7).

The problem of salt accumulation or extrusion by halophytes - in relation to their potential as an NaCl accumulator in a CELSS - is that the NaCl is tolerated or accumulated from relatively concentrated solution, rather than from dilute solution. Also, the natural halophytes are not known for their edible qualities so that their growth would probably not contribute to food production. Even though Na may be beneficial to, or even required by, some halophytes, their uptake of Na is not marked. In one survey (7), Na was found to be the least absorbed by halophytes of the cations studied, being less than that of Li and Mg. It was noted (7) that the roots of barley, which is the species that have been successfully cultivated in sea water irrigation of a strain bred for salt resistance (14,15), have a relatively low affinity for alkali metal cations.

The difficulty in finding a Na accumulator plant

probably stems from the fundamental mechanisms of ion absorption and transport by plants. A distinction must be made between ion uptake by diffusion and cation exchange and by metabolic transport (2). The former mechanisms operate by the mass action laws of the inorganic world and lead to a distribution of ions in the plant tissue directly related to, but lower than, the concentration of ions in the source reservoir (nutrient solution). Metabolic transport, however, controls ion access to the interior of the plant cells and is an "active transport" mechanism that brings into the cells the ions needed for metabolism and growth, even though such transport is against a concentration gradient. Thus, a characteristic feature of marine halophytes is their ability to accumulate K rather than Na from sea water (7). Since Na is not one of the essential elements for most plants (Table I), there can be no metabolic transport mechanism to accumulate Na from a lower to a higher concentration. Possible exceptions are the "obligate halophytes" which require Na, although no literature citation of a case of Na accumulation has been found in this preliminary study. Contact with active research workers in the field of hydroponic growth (26) has, to date, not uncovered any awareness of a plant which concentrates Na from dilute solutions.

G. Overall Justification for Mineral Control in a CELSS

As the capacity for food production will always be limited in a CELSS, it is important to provide optimum conditions for higher plant growth within the constraints of the CELSS environment. The only way to achieve optimum growth and productivity of edible material for the higher plants is to have a nutrient solution within the right range of ionic species and concentrations at all times. In a recycle system this means that there must be control, in terms of removal of ionic species present in too high a concentration and addition of ionic species present in too low a concentration. Such removal and addition cannot be done in a recycle system without processes for mineral separation, removal, recovery, and,possibly, conversion to other oxidation states or ionic forms. Humans on board, as well as plants, require a variety of minerals in what is generally thought of as a minimum quantity, but also should not exceed a toxicity value for some species. Although the minimum amount of many mineral species required by humans will be achieved by consumption of plant edibles containing the minerals, the minimum and toxic values for humans for each element are not the same as for plants. The impact of this fact is that a mineral separation and recovery system may have to accomodate a differing recycle loop for the higher plants and the humans. If the CELSS should have animal species on board further consideration would have to be given to their place in the recycle loops, and to their impact on mineral separation needs.

II. CELSS SCENARIOS WITH AND WITHOUT MINERAL SEPARATION

Any scenario with a plant growth, human consumption, and a recycling of material needs mineral control and separation; although the emphasis and importance may vary with the food production and waste processing subsystems and the degree of closure of the recycle system.

In order to be more specific about the need for mineral separation, prior data which had pertinence to higher plant growth in a closed life support system scenario was perused and an attempt was made to compare data and estimates from various sources. Table VIII shows phytotron plant growth data for food production from seven sources, some of which are actual test data and some of which are scenarios for a CELSS. The Bios-3 data is really the only test data presently available for a comprehensive series of tests on a partially closed life support system. The Cornell and S.A.E. data come from reports featuring a CELSS type scenario. The Calabasas, Israel, Resh, and Johnson data was not concerned with life support systems, but represents observed or recommended parameters for food growth in a soilless culture of finite area.

The number of men supported in Bios-3 was 3 and the Cornell scenario was 24, and the S.A.E. scenario was 10 in the cited report. The phtytotron volume for Bios-3 was given, whereas the Cornell reference said no estimate was made because it was beyond the scope of the report. No volume was given in the S.A.E. report, although this could be somewhere in the program documentation. Sowing areas were given for Bios-3 and the Calabasas test, while the other numbers are just the unit area numbers in the recommendations for hydroponic growth. A critical value for trade-off considerations, the volume of nutrient solution per unit sowing area, was not given for Bios-3, but a reasonable value for a controlled cultivation experiment by the same researchers was given, and was used in Table VIII.

The volume of the nutrient solution was given for the Calabasas test. However the total nutrient solution volume for Bios-3 is the product of sowing area and volume per unit sowing area, while for the Calabasas test the solution was flowing fairly rapidly and the volume given corresponds to one days growth of higher plants. Data on edible mass grown per day is given for a breakdown of wheat and vegetables for the Bios-3 test and the S.A.E. scenario. The Cornell scenario data is for total edible mass, while the various hydroponic growth recommendations are best compared in cucumber yields. Inedible yields are given only for Bios-3 and the Cornell scenario.

Even though these comparisons are less than satisfactory, it is felt that, to a first approximation, any edible and inedible mass comparisons would be helpful in a

TABLE VIII - PART 1

Closed Life Support System Scenario Data

I.D. of test:	Bios-3	Calabasas	Israel	Resh	Johnson	Cornell	S.A.E.
No. Men supported	3	-	-	-	-	24	10
Volume of phytrotron, m3:	157.5	not given	-	-	-	no estimate	not given
Sowing area, m2:	40.8 (33 wheat) (7.2 veg.)	30.4	1000(h)	4047(h)	.0929(h)	no estimate	not given
Nutrient solution per m2, L:	15 (a)	230	-	-	-	-	not given
Total nutrient solution volume, L	606 (b)	39993	-	-	-	no estimate (785 L new/day)	not given
Higher plant production, g/day of							
edible: (dry)	628 total 517 wheat 111 veg.	1342 (e)	116700 (f)	34796 (f)	194.4 (f)	13680	3850 total 3070 wheat 780 veg.
inedible: (dry)	1318 total 1203 wheat 115 veg.	-	-	-	-	11321	not given
total (dry):	1948 total 1720 wheat 227 veg.	-	-	-	-	25001	not given
Production intensity, g/day/m2							
(vegetables)	15.4	-	-	-	-	-	not given
(cucumbers)	4.4	44.1	116.7	8.6	18.1	-	

TABLE VIII - PART 2

Closed Life Support System Scenario Data

I.D. of test:	Bios-3	Calabasas	Israel	Resh	Johnson	Cornell	S.A.E.
% of daily food intake supplied by phytotron:	19 (c)	-	-	-	-	84	various scenarios
Minerals supplied to phytotron, g/day:	260 (dry) 343 (with (hydration)	18760 (g)	-	-	-	1192	-
Minerals supplied to men (in addn. to food), g/day:	0 (d)	-	-	-	-	360 NaCl	-
Author	Gitelson et al.	Berry et al.	Schwarz	Resh	H.Johnson	Nafis/Sze (Schuler)	Spurlock /Modell
Reference	28,29	21,27	4	1	30	31	32

Notes:

(a) volume for Bios-3 not given, figure taken from controlled cultivation experiments by same authors (27)

(b) from (a) * sowing area

(c) 19% = % of dehydrated food needs (by weight) supplied by phytotron, Bios-3 phytotron supplied 26% of carbohydrates, 14% of protein, and 2.3% of fats

(d) in controlled cultivation experiment (27) same authors state that 03-0.4 Kg dry bio-mass/day can supply one man with all P, K, Ca, Mg, S, Fe, and N, but not NaCl

(e) equivalent cucumber yields, assuming edible (fruit) at listed yield (10000 Kg/yr) and 95.1% water

(f) cucumbers only

(g) N, P, K only, calculated from (19) data

(h) unit area for information given in ref., not actual test area

preliminary consideration of the mass of nutrient solution and minerals needed for a phytotron for a CELSS. The bottom line of Table VIII - Part 1 shows a comparison of food production intensities from the various data sources, where cucumbers are the edible food example as data is presented by a number of sources. It is seen that the intensity of cucumber growth for Bios-3 was considerably less than the overall vegetable growth, the Calabasas test with flowing secondary sewage effluent gave much higher yields per unit area, the predicted yields for hydroponic growth in Israel are much higher still, while a book on hydroponic growth and an article on hydroponic cucumber growth predict more modest yields. There is, indeed, a wide variation in this data.

Table VIII - Part 2 shows that Bios-3 supplied, roughly, 19% of the food mass intake to 3 men, while the Cornell scenario anticipates 84% for 24 men. In Bios-3 the minerals were not recycled, but were added to the hydroponic solution as needed. Two figures are given, as it was found necessary and practical to add some minerals with water of hydration included. For the Calabasas test, the weight of minerals included in all the influent nutrient solution to the phytotron has been shown, as this is the actual mineral input for the tests. The Cornell scenario anticipates some mineral addition and some recycle. A figure is given for additional minerals supplied to the men, almost entirely NaCl, as this is given in the Cornell scenario. In the Bios-3 test, adequate minerals, including NaCl, apparently came from a combination of the 19% edibles grown on board and the 81% supplied from the outside.

In Table IX, the data of Table VIII is presented on a one man day basis for calculated total nutrition for the the Bios-3 test and the two scenarios, so that the amounts for nourishment and waste in a CELSS can be more easily compared. Only the Bios-3 test gives complete data. It is realized that this is a simplification of the actual total needed for complete nourishment of one man, but it is still instructive to consider the range of figures calculated for this approximation. For example, the amount of both edible and inedible from the Bios-3 tests comes out considerably greater than the scenario estimates.

Finally, in Table X, scenarios are given for four CELSS with various combinations of phytotron support and mineral recycle. The full recycle scenario is illustrated in the loop shown in Fig. 2. A 10 man - 10 year scenario was chosen, as in the S.A.E. report (Table VIII). Due to the limited availability of data, approximations had to be made in this treatment, and these are defined in the footnotes of Table X. The situations treated are (a) 80% of human nutrition supplied by a phytotron with mineral recycle, (b) 100% of human nutrition supplied by a phytotron with mineral recycle, (c) all human nutrition from stores, and (d) all human nutrition supplied by a phytotron but all minerals

TABLE IX

Comparison of Phytotron Utilization Calculated for One Man Day

Total Nutrition *

I.D. of test:	Bios-3	Cornell	S.A.E.
Volume of phytotron, m3:	276	no estimate **	not given ***
Sowing area, m2:	72 total 59 wheat 13 veg.	no estimate **	not given ***
Nutrient solution volume, L:	1063	no estimate **	not given ***
Higher plant production, g/man day of			
edible: (dry)	1102 total 907 wheat 195 veg.	679 total	385 total
inedible: (dry)	2312 total 2110 wheat 202 veg.	561 total	not given ***
total (dry):	3414 total 3017 wheat 397 veg.	1240 total	not given ***
Minerals supplied to phytotron, g/day:	456 dry 602 hydrated (no recycle)	59 dry (with recycle)	not given ***
Minerals supplied to man (in addn. to food) g/day:	0	15	not given ***
Reference	28,29	31	32

* (amt. given) / (no. of men supported * fraction of nutrition grown in phytotron)

** this data beyond scope, according to reference

*** data not given in reference, but may be in documentation

TABLE X - PART 1

Scenario Data for a CELSS

	80% human nutrition supplied by phytotron (recycle minerals)	100% human nutrition supplied by phytotron (recycle minerals)	0% human nutrition supplied by phytotron	100% human nutrition supplied by phytotron (all stored minerals)
No. men supported	10	10	10	10
Length of mission, yrs.:	10	10	10	10
Volume of phytotron, m3 (a):	1363	1705	0	1705
Sowing area, m2 (b):	353	441	0	441
Nutrient solution volume, L, or wt., Kg (c):	5297	6621	0	6621
Higher plant production, g/day of edible (d): (dry)	5432	6790	0	6790
inedible (e): (dry)	11400	14250	0	14250
Stored food, Kg (f):	4557	0	24783	0
Total phytotron product g/day (dry) (g):	16832	21040	0	6790
Mineral elements from phytotron product processed/day, g, (h):				
N (15000 ppm):	252	315	0	0
P as PO4--- (9000 ppm):	152	1891	0	0
K (80000 ppm):	1346	1683	0	0
Ca (20000 ppm):	337	420	0	0
Mg (4000 ppm):	67	84	0	0
Fe (100 ppm):	2	2	0	0
Zn (40 ppm):	1	1	0	0
Cu (6 ppm):	0.10	0.13	0	0
Mn (50 ppm):	1	1	0	0
Mo (2 ppm):	0.034	0.040	0	0
B (49 ppm):	1	1	0	0
S as SO4-- (1000 ppm):	17	21	0	0
Cl (100 ppm):	2	2	0	0
total g/day(exc. Cl):	2175	2717	0	0

TABLE X - PART 2

Scenario Data for a CELSS

	80% human nutrition supplied by phytotron (recycle minerals)	100% human nutrition supplied by phytotron (recycle minerals)	0% human nutrition supplied by phytotron	100% human nutrition supplied by phytotron (all stored minerals)
Mineral elements for humans,g/day (i),				
Na:	60	60	60	60
NaCl:	150	150	150	150
NaCl build-up in nutrient solution without separation, (j) ppm,				
1 day:	28	22	-	-
2 days:	56	44	-	-
10 days:	283	221	-	-
30 days:	849	663	-	-
6 mo.:	5168	4031	-	-
1 yr.:	10336	8063	-	-
NaCl storage if no recovery, Kg (k):	547	547	547	547
Mineral elements supplied by recycle or storage for phytotron, Kg (l):	7942 (recycle)	9917 (recycle)	0	9917 (storage)
Minerals needed as per Bios-3 data base, Kg (m):	8214	10267	10267	10267
Supplies to bring on mission , Kg (n)				
nutrient solution:	5297	6621	0	6621
stored human food:	4557	0	24783	0
NaCl for humans:	0.15	0.15	547	547
Stored minerals for plants, Kg:	0	0	0	9917
Total stores:	9854	6621	25330	17085
Equipment needed for mineral recycle,Kg (o):	960	1110	0	0
Total of stores and equipment, Kg:	10814	7731	25330	17085

TABLE X - PART 3 (footnotes)

(a) volume phytotron, m3 = [{g edible per man from (31)} / {g edible per man from (28)}] * [{volume phytotron, m3, from (28)} / {No. men in (28)} * {fraction nutrition supplied in (28)}] * [{fraction nutrition supplied by phytotron in this scenario} * {No. men in this scenario}]

(b) sowing area, m2 = [{g edible per man from (31)} / {g edible per man from (28)}] * [{sowing area from (28), m2} / {No. men in (28)} * {fraction nutrition supplied in (28)}] * [{fraction nutrition supplied by phytotron in this scenario} * {No. men in this scenario}]

(c) volume nutrient solution, L or Kg = {sowing area, m2} * {volume solution per m2 sowing area from (29)}

(d) edible produced, g/day = {g edible per man from (31)} * {fraction edible supplied by phytotron in this scenario} * {No. men in this scenario}

(e) inedible produced, g/day = {g edible per man from (31)} * {ratio of inedible to edible produced in (28)} * {fraction nutrition supplied by phytotron in this scenario} * {No. men in this scenario}

(f) stored food, Kg = [{g edible per man from (31)} - {g edible produced by phytotron in this scenario}] * [No. days of mission] / [1000]

(g) total phytotron product per day, g = g edible (d) + g inedible (e)

(h) mineral elements recycled, g/day = {ppm value in range given for dried plant tissue in Table V} * {g phytotron product per day (g)} / {1000000}

(i) mineral elements needed for humans, g/day = {estimate 15 g NaCl per man-day (1.5 L liquid excretion at 10 g/L conc. Na/Cl} * {No. men on mission} * {(for Na only) ratio of atomic wt. Na and molec. wt NaCl}

(j) NaCl build-up if no recovery, ppm = [{g/day for humans (i) * {No. days}} / {Kg nutrient solution (c)} * {1000}] * [1000000]

(k) NaCl storage if no recovery, Kg = [{g/day for humans (i)} * {mission length, days}] / [1000]

(l) mineral elements supplied by recycle, Kg = [{g total from plant production recycle (h)} * {No. days mission} / [1000]

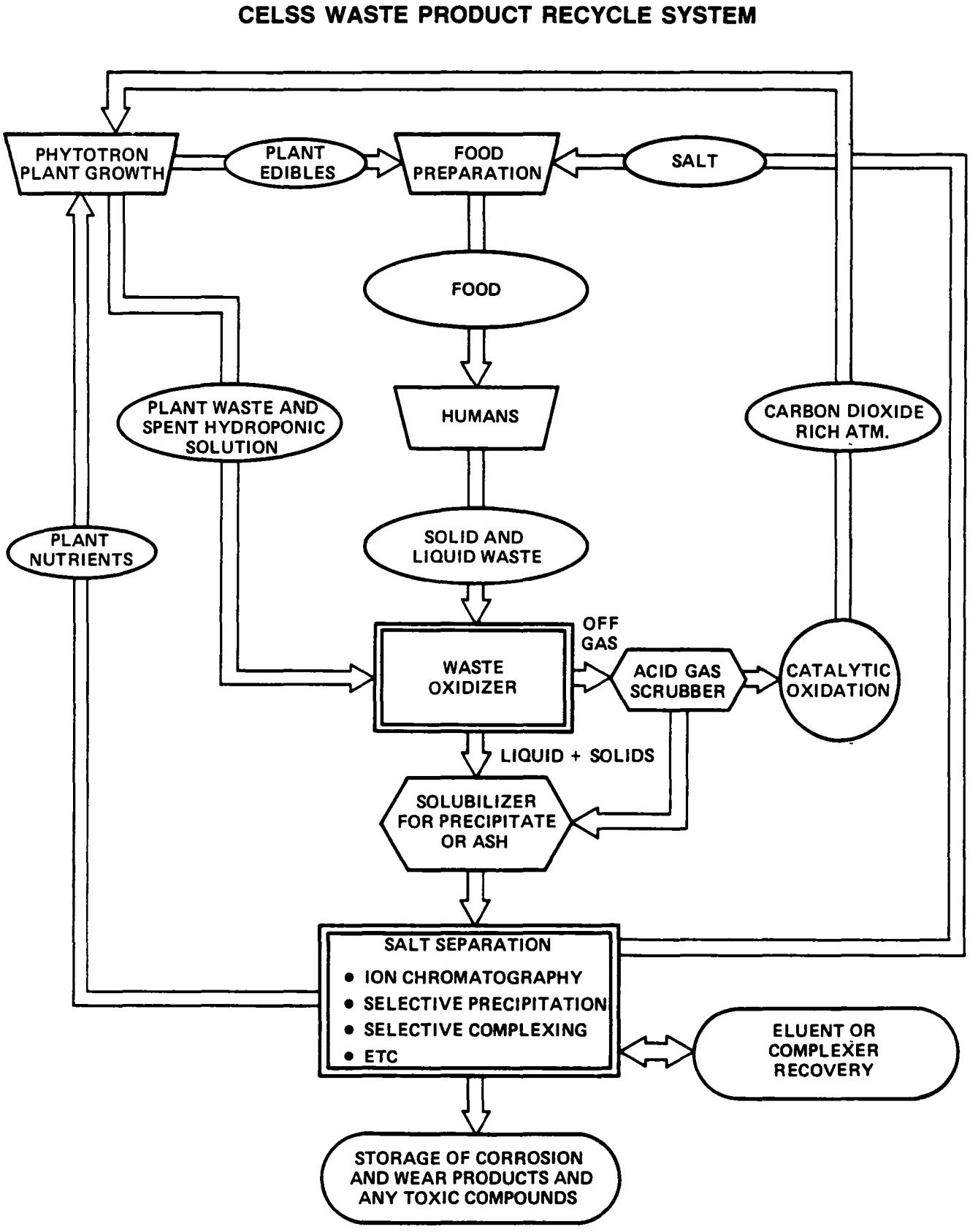
TABLE X - PART 4 (footnotes)

(m) mineral needed as calculated from Bios-3 data base, Kg = [{g edible per man from (31)} / {g edible per man from (28)}] * [{g/day minerals (dry) supplied to phytotron from (28)} / {No. men in (28) * fraction of nutrition supplied in (28)}] * [fraction nutrition supplied in this mission] * [No. men in this mission] * [No. days of mission] / [1000]
- note: this calculation from different data base (actual amount minerals supplied in Bios-3 test and agreement with amount calculated from data base of (1) (amount minerals found in dried plant tissue and estimated edible amount needed and inedible amount accompaning) is satisfactory

(n) supplies to bring on mission (mineral nutrient solution and stored food only), Kg = Kg nutrient solution (c) + Kg stored food (f) + Kg minerals for humans (only 1 day NaCl needed for recycle scenarios)

(o) equipment needed, Kg = [{12 L/man estimate for ion-exchange chromatography mineral separation scenario (33)} * [ratio of {(inedible material produced by phytotron in (28)) * (fraction of nutrition supplied by phytotron in this scenario)} to {edible material produced by phytoron in (28)}] + [12 L/man (representing minerals in edible portion produced by phytotron + mineral in balance - if any - of nutritional needs for humans supplied by stored food)] * [No. men on mission] * [2 Kg/L estimated column density] + [Kg estimated for eluent (in column and eluent recycle loop = {total L for ion-exchange column for recycling minerals (edibles + inedibles)} * {1 Kg/L density}]

Figure 2


CELSS WASTE PRODUCT RECYCLE SYSTEM
PHYTOTRON PLANT GROWTH
PLANT EDIBLES
FOOD PREPARATION
SALT
FOOD
HUMANS
PLANT WASTE AND SPENT HYDROPONIC SOLUTION
CARBON DIOXIDE RICH ATM.
PLANT NUTRIENTS
SOLID AND LIQUID WASTE
OFF GAS
WASTE OXIDIZER
ACID GAS SCRUBBER
CATALYTIC OXIDATION
LIQUID + SOLIDS
SOLUBILIZER FOR PRECIPITATE OR ASH
SALT SEPARATION
• ION CHROMATOGRAPHY
• SELECTIVE PRECIPITATION
• SELECTIVE COMPLEXING
• ETC
ELUENT OR COMPLEXER RECOVERY
STORAGE OF CORROSION AND WEAR PRODUCTS AND ANY TOXIC COMPOUNDS

supplied from stores.

Phytotron volume and sowing area were calculated from two data sources: the mass of edibles needed for human nutrition was taken from the Cornell report (31), while the volume needed to raise this mass was taken from the Bios-3 report. This was done because Table IX shows that the per person edible needs calculated on the basis of the 19% supplied in the Bios-3 tests comes out high and possibly not representative because of the small proportion of the diet actually supplied by the phytotron. The S.A.E. test estimate (32) is even smaller than that from the Cornell report, and may be allowing too small a margin of safety for a CELSS system. On the other hand, the phytotron volume and sowing area from the Bios-3 test was taken from actual growing experience for a CELSS type situation, and were felt to be the best data presently available to use in a predicted senario. The nutrient solution volume calculation relies on other Russian data connected to the Bios-3 test, and, at least, has a foundation in experiments for a CELSS type test.

The mass of edible material needed comes directly from the estimate of the Cornell test (31). However, inedible mass is calculated by taking the ratio of edible to inedible actually found in the Bios-3 test (28) and is higher than that considered in the Cornell report. The Bios-3 ratio was taken, as it was firm experimental data from a CELSS type test. The estmate of stored food simply considers the proportion needed and the edible mass per person allowed in (31). It is assumed that stored food is 100% edible. The total phytotron product will be the total of the edible and inedible mass.

In order to calculate the mass of mineral to be recycled, a figure was chosen in the range of data given for each element listed in Table V, as the Table V data is the minimum or expected amounts in healthy plant tissue. The ranges are considerable, but the data sources are reliable and it was felt that this was a a valid use of the data for approximating the mineral needs in a CELSS. When combined with the misssion size and length and the % of nutrition supplied by the phytotron, these figures give the total mass of minerals needed for the phytotron, either from recycle or storage. However, as the use of data for dried plant tissue seemed to introduce considerable approximations, a check was made on mineral needs by calculations based on the edible mass needed estimate from the Cornell report, the amount of edible mass supplied in the Bios- 3 test, and the actual mass of minerals added in the Bios-3 test to maintain phytotron production. It can be seen in Table X - Part 2 that the figures calculated from the actual mass of minerals used in the Bios-3 test are in reasonable agreement with the calculation based on the composition of dried plant tissue.

Table X - Part 2 also shows the amount of NaCl consumed by the human crew, based on the simple but reasonably accurate assumption that a human excretes 1.5 L/day of 1% NaCl. If this amount of NaCl is processed into the waste system and to the phytotron without separation, there will be considerable NaCl build-up in any reasonable volume of mineral nutrient for the higher plants. Table VI - Part 3 cites various authors as giving values from 50 to 1000 ppm of NaCl as the upper limits tolerable without inhibiting plant growth or development. In Table VII - Part 2 the lower value is chosen as a control point, as it is believed that optimization of the food production capacity in a given volume would be very desirable in a CELSS. Thus, the figures shown in Table X - Part 2 show that the build-up of NaCl in a CELSS phytotron would be unreasonably rapid without separation and recovery.

At the bottom of Table X - Part 2 a comparison is made of the the mass of materials needed for the food supplied in the various scenarios considered. This shows that the 10 man - 10 year mission would need about 10,000 Kg of stores for total human nutrition and plant nutrition for a phytotron supplying 80% of human nutritional needs and about 7,000 Kg for a phytotron supplying 100% of human nutritional needs. This compares with about 25,000 Kg needed with no phytotron, and 17,000 Kg needed for a phytotron with no mineral recycle. It is recognized that the masses of stored food and phytotron grown food would have different nutritional values due to probable differences in the choice and composition of food items. However, for a first approximation applied to these calculations, equal dried masses of any food mixtures are considered to be of comparable nutritional value. Allowance for balanced nutrition in diets is a perturbation of the mass figures and could be calculated in a more intensive study.

Since mineral separation and recycle cannot be done without some equipment and, probably, chemicals, a calculation was also done to give some order of estimate on these factors. The only readily available estimate of equipment was for mineral separation by ion-exchange chromatography, where it was calculated that a resin column of about 12 L/man should allow separation of K and Na (33). For Table X, an allowance was made for eluent mass, with the assumption that eluent recycle would also be used to minimize eluent volume. The total adds about 1000 Kg (Table X - Part 2) so that the mineral recycle modes still are considerably more attractive from a stored mass point of view than the modes without a phytotron or with a phytotron but without mineral recycle.

Other means of mineral recycle may be added or chosen to replace ion exchange chromatography, but data is not available at present on the masses of equipment or of reagents needed. In any case, the Table X figures show the

general mass range in which such control and separation methods should operate in a CELSS. Longer missions than that used in the calculations should make any recycle mode more attractive. Larger crews are a more complex consideration, but generally favor recycle modes because of lower total launch weight, less capital equipment per man for recycle operations, and availability of a more specialized labor pool for recycle operation and maintenance tasks.

In considering a mineral recycle scenario, the exact placement of the mineral control and separation facility or sub-system or sub-systems in the mineral recycle loop was not considered, although it would proably handle input from the waste oxidation unit effluent and direct output to the mineral nutrient solution for the phytotron. In the general picture available at this time, it is considered that mineral control and mineral separation processes are independent of position in the mineral flow loop.

III. SEPARATION METHODS

Many separation techniques used for inorganic ions have been primarily developed for the separation and identification of traces of inorganic ions, the separation of ions with very similar chemical properties (e.g.the rare earths), or the removal of a certain class of inorganic ions (e.g.the heavy metals). Although all separation techniques should be considered, the following appeared, from a preliminary literature survey, to have potential for the separation of the mineral species to be expected in a CELSS waste processing system: (1) ion-exchange, high pressure, and continuous chromatography, including rotating annular beds, rotating disc chromatography, and gel permeation chromatography, (2) fractional crystallization, (3) flotation, foaming and frothing techniques, (4) membrane separation processes, (5) cyclic separation processes and (6) non-chromatographic ion-exchange processes.

Following is a brief compilation of recent separations work in these fields, with comments on its pertinence to mineral separations in a CELSS.

(1) Chromatography: There has been a great deal of work on chromatographic separations on ion-exchange resin columns which has shown that the technique is applicable to the analytical separation of a wide range of inorganic cations and anions, including the alkali metals and the alkaline earth metals (34-48). An early use of ion-exchange resin column chromatography was rare-earth separation (49,50). This work was developed into considerable scale-up, involving the separation and recovery of substantial quantities of metals such as neodymium (51), praseodymium (51), and yttrium (52).

Interest in synthetic inorganic ion-exchange materials (e.g. antimonic acid and stannic phosphate) has been heightened by their superior stability to high temperature and ionizing radiation (53). These inorganic materials are also known to have higher ion-exchange selectivities for certain elements than organic ion-exchange resins. They are candidates for further investigation of their application to separations of the type and scale needed in a CELSS.

There has been considerable interest in high pressure chromatography on ion-exchange resins, including assessment of the column capacity factors for the alkali metals and magnesium at pressures up to 60,000 p.s.i. (70). The high pressure chromatographic separation of lanthanides and trivalent actinides has been reported (54). An ion-exchange chromatographic technique suitable for operation at modest pressures (30-150 p.s.i.), and in a continuous mode, uses a rotating annular bed and has been applied to Cu-Ni-Co, Fe-Al, and Zr-Hf separations (55). This appears to be a powerful technique for mass separation and recovery as the

authors estimate that a "continuous annular chromatograph" unit 60 cm diameter x 60 cm long could separate and produce 50 metric tons per yr. of Zr containing <0.01% Hf (2.5% of the U. S. demand for this metal)."

High pressure or "high performance" liquid chromatography, called "HPLC", generally refers to liquid-solid chromatography, where the liquid is a solution of the constitutents to be separated in one or more solvents and the solid is finely divided silica, alumina, porous polymers, porous glass, and other materials. The most common detectors are ultra-violet absorption and refractive index. Reviews of this separation technique, emphasizing biochemical and biomedical applications has been published (56,57,58).

Liquid chromatography is the focus of a great deal of current technology and sophisticated apparatuses for HPLC are currently marketed by a variety of manufacturers (59-68). The preponderance of the data presented and applications suggested for HPLC is for the separation or preparation (69) of complex organic and biochemical materials. The use of high pressures for inorganic mineral separations on ion-exchange resins has also been shown to be feasible (54,55,70), as mentioned above. However, the abundance of current technology in HPLC, and the rapid advances in techniques and application make it a technique of interest for modification to allow application to mineral separation.

A modification of thin layer chromatography, known as "rotating disk thin layer chromatography" (71), allows faster separations and greater sample volumes than the conventional technique. A commercial rotating disc instrument (72) is available as a preparative liquid chromatograph.

Permeation chromatography on gels, such as polyacrylamide, appears feasible for strong electrolytes, and worth some consideration for a CELSS. The separation mechanisms have been discussed (73), and distribution coefficient data have been obtained for a number of inorganic cations and anions (74). In one work (74), the distribution coefficients of KCl, NaCl, and other salts were measured on polyacrylamide gel. The technique appeared marginally applicable to KCl/NaCl separation, due to the closeness of their distribution coefficients.

(2) Fractional crystallization: The crystallization of NaCl of various degrees of purity for domestic and industrial purposes has been discussed (75). The incorporation of bivalent heavy metal ions into alkali halide crystals grown in solution (76), including the crystallization of NaCl with Pb++ (77), has also been noted. The effectiveness of crystalization rate and initial salt

concentration on the separation of impurities by NaCl crystallization has been studied (78), as well as the effect of salting out by KCl on the lattice constants of NaCl (79). The cause and solution to the problem of incrustation in an NaCl crystallizer has been discussed (80) and the change in the crystal character of KCl with degree of supersaturation has been noted (81).

The kinetics of NaCl and KCl crystallization in the presence of PbCl2, MnCl2, CdCl2:H2O, and other impurities, has been studied (82), as well as the crystallization of KCl by "coupled crystallization" with NaCl (83). There has been considerable recent work on crystallizations involving NaCl and KCl, and it appears from a phase diagram that some separation of NaCl and KCl and possibly other salts can be achieved by collective crystallization (84). Investigations should be done to see if such separations can be done without adverse effects from mixed crystal precipitation and impurity occlusion.

(3) Flotation, foaming and frothing techniques: These techniques are useful in the separation of insoluble particulates and colloidal materials as well as soluble ionic species. A surfactant must generally be added to the mixture to be treated. A critical review (85) of collector mechanism research in flotation treats two classes of systems, sulfides and non-sulfides. The latter includes oxides, silicates, alumino-silicates, polar salt-type minerals containing alkaline earth cations, and soluble salts. The flotation of halite (NaCl) and sylvite (KCl) from their saturated solutions is discussed. Collectors, such as long-chain amines or salts of long-chain fatty acids must be added to achieve flotation and separation.

A discussion (86) of ionic species separation by "ion flotation" points out that this technique has been applied to the separation of Al and Be, the removal of trace Sr from aqueous solutions, the flotation of acid chromate, and the flotation of cyanide complexes by ferrous ion. It is pointed out that the commercial applicability of virtually any flotation process depends on the recovery and reuse of the surfactant, which would also apply to the usefulness in a CELSS. A process called "adsorption colloid flotation" has been used for the separation of copper and zinc from sea water (87).

An extensive review of separation by flotation (88) differentiates between ion flotation, foam fractionation, precipitate flotation, adsorbing colloid flotation, and froth flotation. The treatment of industrial waters, laundry wastes, domestic sewage, and sea water are mentioned as promising areas for large scale application of flotation techniques. Specific examples are foam fractionation of Zn+2 and Cr+6, removal of Cd+2 from wastewater, flotation of dichromate ion, and removing emulsified petroleum from sea

water. A magnetic field was found to aid in Ni-Co-Cu separation by ion flotation. In other work (89), a theory of selectivity in foam fractionation of Sr++ metallic ions was confirmed by experimental data on UOsub2++ separation. One advantage of foam separation techniques, in many applications, is their ability to selectively concentrate materials from very dilute solutions (90). Anions can be separated by foam separation, using a cationic surfactant (91).

The techniques of flotation and foaming certainly seem applicable to a wide range of mineral separations. However, there is almost always a need for surfactant addition, which, in a CELSS system, means surfactant recovery as well.

(4) Membrane separation processes: Membranes show some selectivity for dissolved solutes, but the permselectivity of water swollen polymer membranes is a complex function of membrane hydration, solute size, solute charge, pore size, and membrane charge (92). Heavy metal ions can be separated from acid mine waters by reverse osmosis with cellulose acetate membranes (93,94,95). Ultrafiltration can be used ,in combination with chelating agents, for heavy metal ion separation and removal (96).

In general, membrane techniques are applicable for separation of dissolved ionic solutes from aqueous solution, but are limited in their discriminatory power for the separation of one disssolve ionic solute from another. For example, Na+ and K+ are separated with difficulty, while the separation of multivalent species from monovalent species is more feasible. Therefore, the use of membrane techniques for the removal of toxic elemental species or corrosion and wear products in a CELSS should be given further consideration.

(5) Cyclic separation processes: Cyclic separation processes have been reviewed (97), and the chief methods of interest were parametric pumping and cycling zone separation. The chief experimental difference in these methods is that parametric pumping uses oscillating flow through an adsorbent bed (98), while in cycling zone separation the fluid is pumped in one direction through a series of beds (99). Considerable mathematical modeling has been done for both methods (98,99,100), and both methods have a potential for continuous multicomponent separation. The experimental work on batch fractionation of ionic mixtures by parametric pumping (101) seems most pertinent to a CELSS. In this work, the adsorbent bed temperature was the controlled thermodynamic variable, and solutions of KCl and HCl were separated by large factors (2000:1). When NaCl was added, to make a ternary solute system, good separation was again achieved. The NaCl stayed in the sorbent bed (ion-exchange resin) while the other solutes migrated to the reservoirs at either end of the bed. The feasibility of a continuous process and multisolute separation was predicted

(100,101), but reports of experimental tests of these possibilities have not been uncovered. In an earlier work (102) parametric pumping was tested on a solution of NaCl, KCl, and HCl with pH as the controlled thermodynamic variable. Some separation of Na+ and K+ from H+ was achieved, but no separation of Na+ from K+ was noted.

The advantage of parametric pumping or cycling zone separation to mineral separation in a CELSS is that, with temperature as the controlled variable, no added chemical species are needed to assist in the separation, or to elute the components, or to regenerate the separating medium. To this factor is added the potential for continuous multicomponent separations. The attactive features must be balanced against an energy expenditure of unknown magnitude, uncertain weight and volume requirements for the system, and a paucity of experimental background on mineral separation with cyclic processes.

(6) Non-chromatographic Ion-exchange separations: Ion-exchange materials can be used in methods and techniques that supplement those mentioned with ion-exchange chromatography. One is the use of combined ion exchange and solvent extraction (103). It was proposed that such separations can be performed "virtually automatically" with solvent recovery by distillation or partition in the presence of salting-out agents. Sequential anion and cation exchange processes have been used for the kilogram scale purification of americium (104). Rapid removal of ions from solution has been achieved by the addition of finely ground ion-exchange particles, followed by coagulation by addition of suspensions of oppositely charged solids (105).

A strong acid ion-exchange resin bed has been used to remove cationic radionuclides dissolved during the decontamination of equipment in a nuclear power station (106). Other large-scale uses of ion-exchange resin beds have been reported in the demineralization of the water feed for electric power generating station boilers (107), treatment of effluent water from an ammonium nitrate fertilizer plant (108), and the treatment of acid mine drainage water (109). The magnitude of water treatment in each of these facilities was in the 50,000-500,000 gallons per day range. Ion-exchange beds in a generating station (107) treated up to 3,000,000 gal. water per cu. ft. resin bed before resin replacement.

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16 Abstract

This report explores the background of the mineral nutrition needs of plants, considers the applicability of mineral control and separation to a controlled ecological life support system (CELSS), and delineates steps that may be taken in a program to analytically define and experimentally test key mineral control concepts in the nutritional and waste processing loops of a CELSS.

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