

ECONOMIC UTILIZATION OF THE LEFT-OVER RESIDUAL BRINES: EMISAL CO. CASE, EGYPT

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ABSTRACT

The left-over residual brines after extracting anhydrous sodium sulphate, halite and epsomite is stored in storage ponds inside EMISAL Co. battery limit and its quantities amounts to about 120000 m³ annually. The waste of left-over brine enriched with economic valuable ions, as boron and potassium of specific gravity up to 1.300 g/cm³. The present study proved the economic possibility of extracting some valuable salts as sodium borates, boric acid and potassium chloride from the waste residual brines and its economic utilization in local markets.

1. INTRODUCTION AND SCOPE:

The left-over (residual) brines often in industrial facilities is disposed back to the sea or in dump areas e.g. abundant salt mines in other cases. Dumping into the sea can harm marine organisms even if done on local and/or on a temporary basis since the residual brines have ion concentrations more than 70-90 times that of the original seawater concentration. In our case, it was found that it is impossible to dispose bittern into Lake Quaroun. This will definitely cause environmental impacts and affect more dangerously on the ecosystem and on the fishing productivity in the lake as compared with seawater because this lake is considered as a closed and isolated basin. Moreover it is against the Egyptian Environmental Authorities law of 2000. This sentence is true since Lake Quaroun is the lowest in topographic level in the depression and suffers from replenishing amounts except for agricultural waste waters replenishing the evaporation rate to maintain constant water level. EMISAL (The Egyptian Salts and Minerals Company) was mainly found to protect the environmental of the Lake from being deteriorated as its water salinity is continuously increasing with time. Salinity of Lake Quaroun water was almost fresh about 150 years ago, but damming projects regulating Nile water loss during flood period into the Mediterranean Sea affect the received amount into the depression. The runoff from the surrounded elevated irrigated fields carrying considerable amounts of salts accompanied with continuous evaporation had led to a steady increase in salinity of the lake water, on average ranges, from 11 ‰ in 1906 up to 31.7 ‰ by 1970 (Meshal, 1973). Now the average salinity reaches 34.342 ‰, EMISAL record (2007), the TDS value was 35.32 g/l and the water density was 1.025 g/cm³. The estimated increase in salinity during the last decade is 0.35 ‰ up to 0.48 ‰ /year.

It was found that the salt content of the lake is increasing with time as the drainage water contributes considerable amount of dissolved salts annually into the lake. Nearly, a volume of water equal to the drainage water is lost through solar evaporation process from the lake, while its dissolved salts remain as well as the dissolved salts of the lake itself (FWMP, 1999 and 2001). The average increase in salinity was estimated to approximately 0.5 g/l/year as mentioned in the theses of Al-Kordy, (2003) and El sheikh, (2004). If salts are not extracted from the lake, the salinity will continue to rise annually

until it turns into a second analog as the Dead Sea with no living organisms causing severe social disturbances.

The feasibility study indicate that the extracted salts are sodium sulphate, followed by sodium chloride and then magnesium salts. The extraction of the designed quantity of salts by “EMISAL” through all stages of production will help in controlling and/or lowering the increase in salinity with respect to time (Fig. 1) and in stabilizing the salinity at Lake Quaroun around the value(s) that keep the bio-diversity of the lake. The bittern can be treated farther to recover magnesium oxide, magnesium hydroxide, and magnesium sulphate or magnesium chloride hexahydrate. This is depending on the initial ionic composition of such bittern. Based on this view (recycling of brines), the feasibility study carried out by EMISAL indicate that the residual brine that pumped out from the crystallizer ponds before harvesting of halite can be utilized to recover the magnesium sulphate hydrate (Epsom salt). Consequently, this will overcome the bittern waste problem. This project represents the third stage of production in EMISAL after the production of anhydrous sodium sulphate and sodium chloride. The design of Epsom salt production project depending on feeding from the mother liquor outlet from the anhydrous sodium sulphate plant, then concentrated from specific gravity 1.190 g/cm^3 to 1.257 g/cm^3 in three consequently ponds prepared for this aim. The obtained results during the study of the brine evolution through progressive solar evaporation in summer season(s) within the crystallization ponds of halite indicated that the brine developed until reaching density of 1.371 g/cm^3 . This resulted in a large quantity of magnesium and potassium salts concentrates were co-precipitated with sodium chloride as contaminations. Thus, the conducted experimental studies on the follow-up of bittern evolution under progressive evaporation were helped in the determination of mineral sequences crystallization limits. So, to avoid the precipitation of magnesium sulphate salts as contaminations with NaCl, the residual bittern should be pumped out from the studied pond before its density reaches the value 1.300 g/cm^3 (i.e. at density equal to 1.285 g/cm^3). This will allow the cutting of 87% of sodium chloride of high purity and also would allow the preservation of all content of magnesium sulphate salts as soluble components within the residual bittern budget.

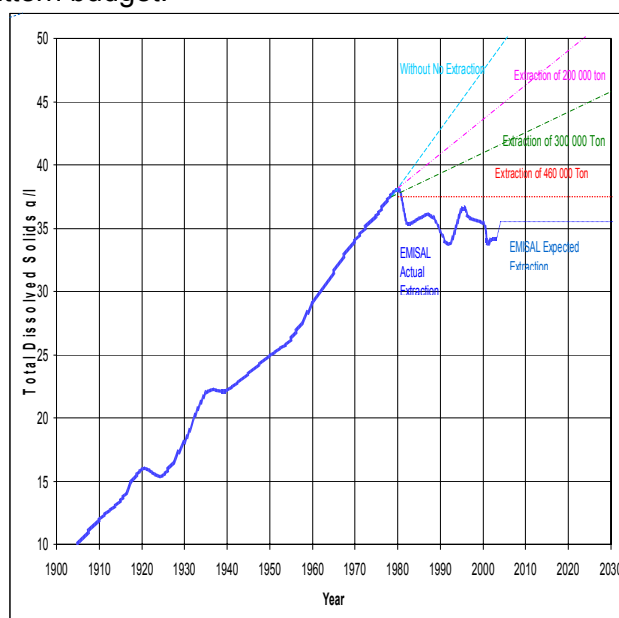


Figure 1: Values of annual salinity values of Lake Quaroun, after EMISAL (2005)

2. Analytical methods and Techniques:

The adopted analytical methods for determination of the different anions and cations are described as follows:

CO_3^{2-} : acid-base titration

K^+ , B^{2-} : atomic absorption (Model GPC 932)

Na^+ : equivalent minus according to ion balance

Mg^{2+} : titration complex metrically with Ca^{2+} by using Eriochrom black T

Ca^{2+} : titration complex metrically by using murexide.

SO_4^{2-} : by barium sulfate precipitation (Dunk et. al., 1969).

Cl^- : titration with silver nitrate using potassium chromate as indicator.

XRD and Transmitted light microscope were applied as to assure mineral composition.

3. RESULTS AND DISCUSSIONS:

3.1. Boron

The average boron content in the waste residual bittern is about 377 ppm, with a total quantity of about 672 ton annually. Extraction of about 843 ton from the estimated quantity of storage waste residual bittern (120000 m³) as sodium borates can be achieved and an amount of about 259 ton of boric acid from the same quantity. A quantity of about 514 ton annually as sodium borates and quantity of about 158 ton annually as boric acid in solid state is possible as to market measures and needs (Tables 1 and 2).

Table 1: Show the chemical analysis of K and B in the studied bittern

		g/l	m mole / Kg	mole Fraction
Sp.Gr.	g/cm ³	1.298	1.298	
T.D.S	g/l	416	416	
CO_3^{--}	g/l	1.35	0.029	0.333
HCO_3^-	g/l	1.7	0.036	0.412
SO_4^{--}	g/l	75	1.013	11.539
Cl^-	g/l	210	7.678	87.430
Ca^{++}	g/l	0.02	0.001	0.007
Mg^{++}	g/l	67.5	3.605	41.047
K^+	g/l	18	0.599	6.821
Na^+	g/l	35.255	1.990	0.868
Other	g/l	7.175		
Hypothetical Salts				
$CaCO_3$	g/l	0.05	0.001	0.007
$MgCO_3$	g/l	1.855	0.026	0.291
$Mg(HCO_3)_2$	g/l	2.039	0.018	0.206
$MgSO_4$	g/l	93.975	1.013	11.539
$MgCl_2$	g/l	186.85	2.545	28.976
KCl	g/l	34.385	0.599	6.822
NaCl	g/l	89.671	1.990	22.655
Others	g/l	7.175		
B	g/l	0.3	0.035	0.403
B as H_3BO_3	g/l	1.691	0.036	0.410
B as $Na_2B_4O_7$	g/l	1.37	0.009	0.101

3.2. Borax

Borax can be extracted from the bittern (Sp. Gr. = 1.300 gm/cm³), where at such density most of halite was precipitated by evaporation.

The bittern is mixed with a chelating agent (Kerosene solution) to remove the borates (sodium borates) from the bittern as emulsion (Robert et. al., 1994). The emulsion must be at pH value between 4.5 and 5.5 to avoid precipitation of other constituents of highly soluble minerals. The emulsion solution at pH 5.5, the boron extraction efficiency reaches about 90%.

Table 2: Show the chemical analysis of K and B in the studied bittern

Sp. Gr. (g/cm ³)	Potassium as "K" (g/l)	Boron as "B" (mg/l)
1.023	0.400	9.2
1.048	0.772	12.8
1.069	1.070	15.5
1.077	1.150	15.7
1.161	2.728	35
1.219	4.251	62
1.185	3.563	65
1.240	7.513	113
1.312	15.92	377.5
1.233	6.788	93.5
1.241	7.073	107.5
1.235	7.273	128.5
1.233	7.074	118
1.350	6.7	395

The emulsion is putting in a settling tank and through separator to break the emulsion and extracting from the bittern. The separating crystals, on the laboratory scale, with fine crystals form were obtained, (Fig. 2). This method is in agreement with Phyllis (1992 and 1995).

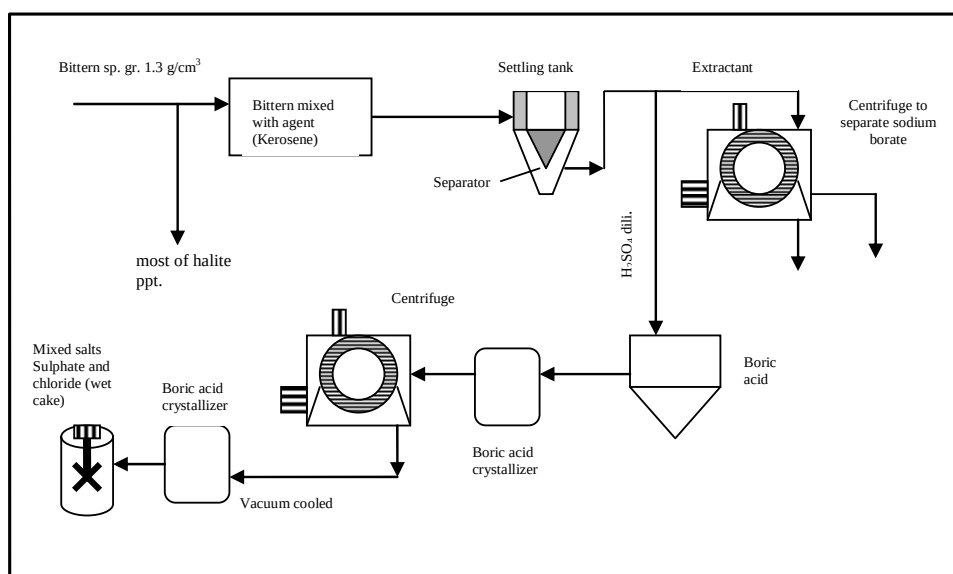


Figure 2: Show the flow diagram of extraction of sodium borates and boric acid

3.3. Solid phase diagram of $\text{Na}_2\text{B}_4\text{O}_7$:

The chemical model of Harvi et. al. (1984) based on the equation of Pitzer and Magora (1973) to calculate the solubility of the quinary system, Na^+ , K^+ , Mg^{2+} // SO_4^{2-} , $\text{B}_4\text{O}_7^{2-}$ – H_2O . The equilibrium solid phases were: K_2SO_4 , Na_2SO_4 , MgSO_4 , $\text{Na}_2\text{B}_4\text{O}_7$ and $\text{K}_2\text{B}_4\text{O}_7$. The phase diagram of the quinary system (Fig.3) indicate that the crystallization fields of MgSO_4 and Mg , Na and K borate minerals are larger, but the crystallization fields of sodium sulphate and double salt $\text{Na}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ are smaller. This feature is very important for the extraction of sodium borate from the studied bittern due to extraction of sodium sulphate from the initial brine and the amount of it in effluent mother liquor brine is little ($\approx 26 \text{ g/l.}$). The behavior of the dissolved borate in aqueous solution is very complex, depending on many parameters as, Eh and pH value, Yin et. al. (2001).

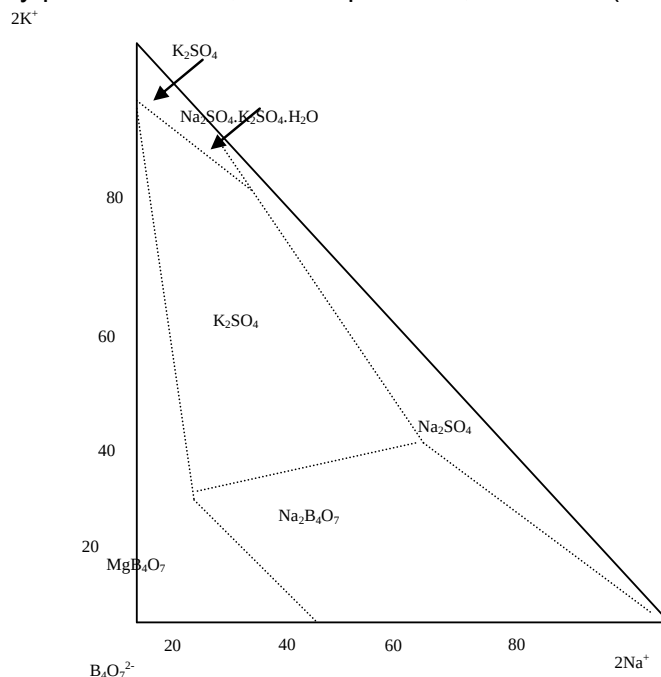
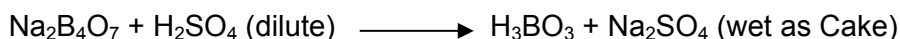


Figure 3: Projected-diagram of the quinary system of Mg^{2+} , Na^+ , K^+ , // SO_4^{2-} , $\text{B}_4\text{O}_7^{2-}$ – H_2O after Yin, et al., 2001 and created the zones of experimental data of studied bittern on it

3.4. Boric acid:

The extraction of boric acid out of the bittern is combined with dilute sulphuric acid to convert the sodium borate to boric acid as follows:



This step produces liquor containing boric acid, magnesium sulphate, magnesium chloride and organic fractions.

The filtered liquor is cooled (vacuum) in a boric acid crystallizer. The resulting boric acid crystals are centrifuged to separate them from the liquor. The resulting liquor is further vacuum cooled to crystallize the mixed salts (sulphate and chloride), which are centrifuged to form a wet cake.

Figure 2 indicates the flow sheet of extraction of sodium borates and boric acid.

X– Ray diffraction patterns confirmed the mineral composition.

Borax solid phase crystals were investigated by polarizing microscopy and chemical analysis as ions and salts.

The polarizing microscopy revealed the small crystals as cubes of sodium borates, (Fig. 4).

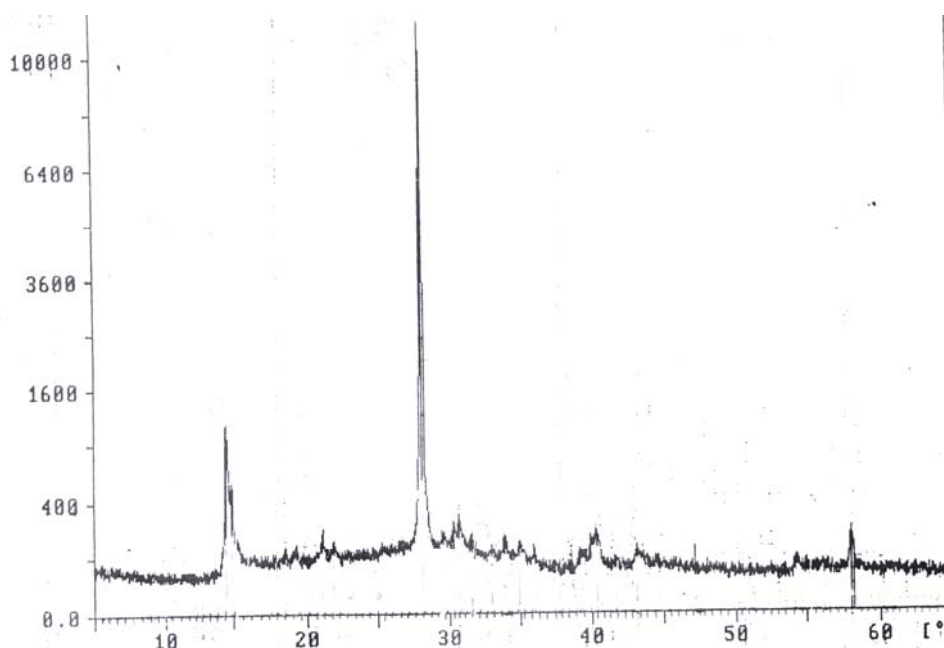


Figure 4: Showing the XRD for the main patterns of the boric acid (H_3BO_3)

3.5. Use of borates

The major uses of borates include: fiberglass insulation, textile or continuous-filament glass fibers, glass, detergents and bleaches, enamels and frits, fertilizers and fire retardants. These uses are according to the U.S. Bureau of mines (1994).

3. 6. Uses percentage as:

Glass products	71%
Soaps and detergents	5 %
Fire retardants	4 %
Agriculture	4 %
Others	16%

3.7. Uses of Borax and Boric acid in Egypt:

- the glass industry
- ceramic glasses
- enamels
- cosmetics
- textiles

The glass and porcelain industries are the major consumers of borax and boric acid, consuming over 50% of the total imported quantity. The imported quantity is not accurate detected.

The boric oxide is used in glass, enamels and glazes it controls thermal expansion, improves durability, assists the melting processes and is also a component of inorganic colours and decorations. (Industrial mineral journal, 2004).

3.8. Current Effluent Waste from Epsom salt plan

The composition of the effluent waste from the Epsom salt plant is showing in table 3. This composition revealed that the waste outlet from epsom salt are mainly contains, Sylvite (KCl), Carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and Bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$). The discharged quantity of the effluent from Epsom salt is $122472 \text{ m}^3/\text{year}$. The economic beneficiation from this waste is mainly in production of Sylvite, Bischofite and Carnallite

- The effluent waste is transferred to a storage solar pond to precipitate halite by solar evaporation, the specific gravity increases from 1.239 gm/cm^3 to 1.295

gm/cm³. This quantity losses 40% of its volume by solar evaporation to became 73200m³

- The residual waste (1.295gm/cm³) is pumped into another storage pond or tank with dilution by fresh water 5% by volume. After dilution, the specific gravity will decreases to reach 1.280 gm/cm³, the diluted waste bittern is cooled down to -20C°, the sylvite (KCl) will be separated. The remains are a complex salts of carnallite (KCl. MgCl₂.6H₂O), recrystallized and leached by water to separate bischofite (MgCl₂ 6H₂O). This agreement with, Classett, (1970), Boutry, (1993) and Fernandez Lozano, (1974 and 1993).

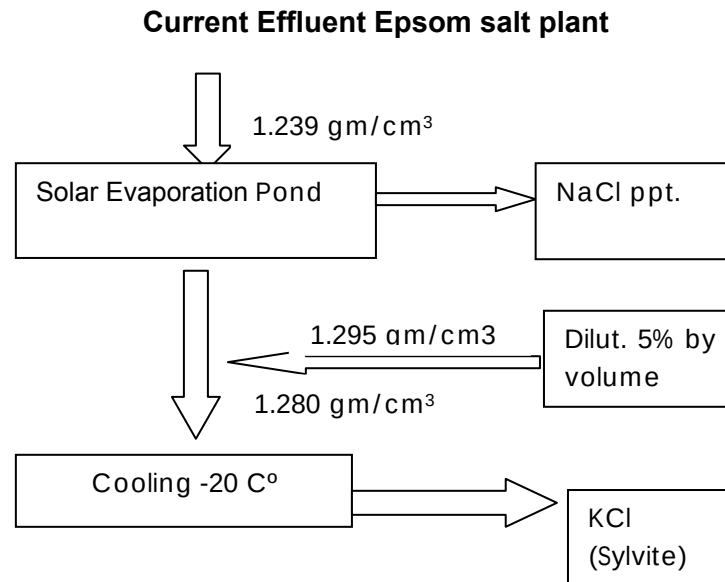


Figure 5: Sylvite Recovery block diagram

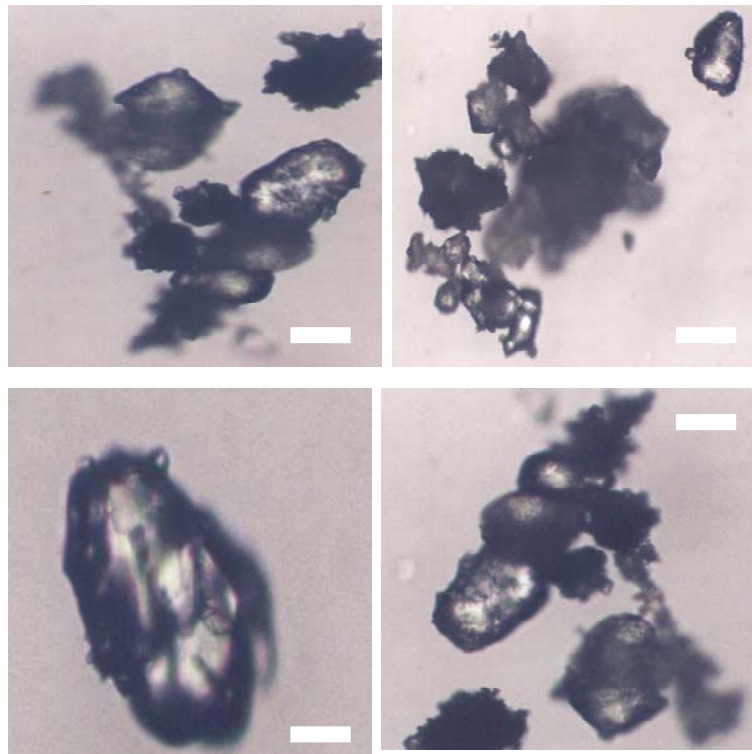


Figure 6: Photomicrographs (A, B and D) showing the crystals of sodium borate (Borax), (C) showing the crystals of boric acid, PL. Bar is 250μ.

The separated solid phase crystals of sylvite were detected by chemical analysis as ions and salts.

Table (4) showing the chemical composition of separated solid phase crystals of sylvite.

SUMMARY AND CONCLUSIONS

The waste residual bittern after extracting anhydrous sodium sulphate, halite and epsomite is collected in ponds called storage ponds inside EMISAL Co. area, the quantity of this bittern amounts to 120000 m³ annually. The residual waste bittern is enriched with high valuable ions (e.g. boron and potassium with specific gravity up to 1.300 gm/cm³). Extract of sodium borates, boric acid and potassium chloride revealed possible. The average boron content in the waste residual bittern is about 377 ppm (Table 5.6), with a total quantity of 672 tons annually. The extraction of 514 tons as sodium borates and 158 tons of boric acid in solid state is feasible. The extracted annual quantity of potassium chloride reaches 2224 tons calculated as K₂O. The method of extracting boric acid and sodium borates were assigned as in Figure 3.

Adopting the chemical model of Harvi et al., (1984) based upon the equation of Pitzer and Magora, (1973) to calculate the solubility of the quinary system, Na⁺, K⁺, Mg²⁺ // SO₄²⁻, B₄O₇²⁻ – H₂O, the equilibrium solid phases were adapted are K₂SO₄, Na₂SO₄, MgSO₄, Na₂B₄O₇ and K₂B₄O₇. The major uses of borates include: fiberglass insulation, textile or continuous – filament glass fibers, glass, detergents and bleaches, enamels and frits, fertilizers and fire retardants. This uses according to the U.S. Bureau of mines, (1994).

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