

AN ELECTROCHEMICALLY REGENERATIVE HYDROGEN-CHLORINE ENERGY STORAGE SYSTEM FOR ELECTRIC UTILITIES*

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Summary

Electrolysis of HCl and storage of hydrogen and chlorine is proposed as a means for energy storage for the electric utility industry. An economic evaluation is presented which shows that the system has a clear advantage over the hydrogen-air storage system and is comparable in cost to gas turbines. The system is flexible, allowing both energy storage and hydrogen production for industrial purposes, and lends itself easily to scale-up. Assuming that the R&D goals of this new system are met, it will compete successfully with all other electric energy storage devices presently considered.

Essential criteria for an energy storage system for electric utilities

The essential requirements of an energy storage system for electric utilities are: (i) high reliability; (ii) low capital cost; (iii) long life (> 20 years); and (iv) high overall efficiency (over 70% electric → electric (*ETE*)). In addition, it is also necessary to consider the load-duration cycle. In the past, load factors have been calculated for daily cycles. It appears more advantageous to consider weekly cycles, because the energy which can be saved during the low weekend demand periods can be stored and used during the peak hours on weekdays. If one considers that about 10% of the energy

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produced by a nuclear power station (capacity of about 1000 MW) will have to be stored, the size requirements of the energy storage system will be quite high.

Energy storage systems in use or under consideration

Pumped storage is the only method of energy storage currently used by electric utilities. It is the most economical and satisfies all the necessary criteria outlined above. Land availability and siting are the most serious drawbacks in expanding this method of energy storage. Underground pumped storage methods are being considered for flat land regions. Use of flywheels or compressed air (in underground caves) is being investigated. Flywheels have yet to be demonstrated in large enough sizes. Compressed air plants will suffer from the same disadvantages as pumped storage, and will still consume fossil fuels.

Several electrochemical systems have been proposed for load levelling purposes in electric utilities. These include lead-acid, lithium alloy-metal sulfide, sodium-sulfur, and zinc-hydrogen batteries, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ - $\text{Ti}^{3+}/\text{Ti}^{4+}$ redox couples and the hydrogen storage systems. The lead-acid battery technology is over a hundred years old. It has a high overall efficiency (*ETE* efficiency > 70%), but this decreases with increasing rate of charging and discharging. It may be difficult to meet, simultaneously, the requirements of deep discharge and long life with these batteries. At the present time, lead-acid batteries have a limited lifetime of about 5 - 10 years. Furthermore, these batteries require considerable maintenance.

With the high temperature systems (lithium alloy-metal sulfide and sodium-sulfur) the main problems are connected with the highly corrosive environment in the cell, which makes it extremely difficult to find long life materials for fabrication of the batteries. The zinc-chlorine system looks attractive because of its high performance (*ETE* efficiency > 70%) at relatively low temperatures (< 100 °C). Problems encountered in the complete regeneration of zinc, dendritic growth and shape change, have to be overcome. Redox systems have the potential of low cost but tend to occupy a large volume. The feasibility of these systems will depend on the development of suitable membranes to prevent mixing of the half-cell constituents. Capital costs and cycle life must be improved in all the above systems to make them economically competitive.

The hydrogen-air system, though attractive from the point of view of weekly cycles and the use of the fuel cell to supply intermediate and peak loads, suffers from the disadvantages of a relatively low *ETE* efficiency (~ 50%) and a high capital cost, mainly because three major components (water electrolysis cell, metal hydride storage and fuel cell) are necessary. The main reason for the inherently lower efficiency of the hydrogen-air system as compared with the other electrochemical systems is the irreversibility of the oxygen electrode reaction. Furthermore, since different electrocatalysts

have to be used for oxygen evolution and reduction, two electrochemical cells are necessary instead of one, as in the case of a battery.

Proposed electrochemically regenerative hydrogen–chlorine energy storage system, its advantages and disadvantages

The loss of efficiency in the hydrogen energy storage system is caused by the sluggishness of the O_2/OH^- redox couple. It can be eliminated by replacing it with a Cl_2/Cl^- redox couple [1, 2]. The proposed electrochemically regenerative closed cycle hydrogen–chlorine fuel cell system will thus involve: (i) using off-peak power to electrolyze hydrochloric acid; (ii) metal hydride storage for hydrogen and storage of chlorine as the liquid; and (iii) combining the hydrogen and chlorine, in the same electrochemical cell operating in the discharge mode, and storing the hydrochloric acid produced, outside the cell. This new system is schematically represented in Fig. 1.

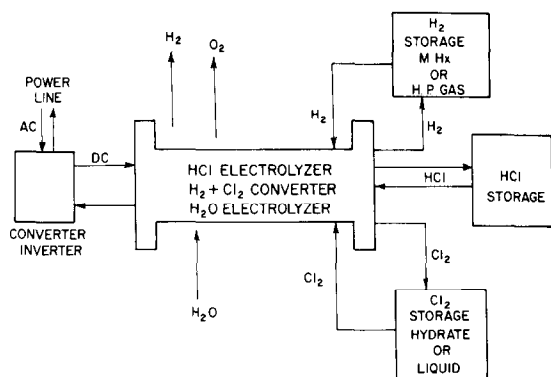


Fig. 1. Schematic of an electrochemical system as an energy storage system for electric utilities and for hydrogen production.

The main advantages of such a system are: (i) the electrode reactions of hydrogen and chlorine are quite reversible. Thus, one can expect an *ETE* efficiency of over 70%; (ii) the same electrodes can be used as electrocatalysts in both charge and discharge modes. Therefore, the same electrochemical cell can be used for both functions, which cuts down the capital costs; (iii) it should be possible to use the same cell in a third function (see Fig. 1) for electrolysis of water, to produce hydrogen and oxygen, using off-peak power. The hydrogen produced could be used for injection into the natural gas pipelines or sold to chemical industries. The hydrogen selling price could be used as a credit against the cost of the hydrogen–chlorine system; (iv) the methods of drying and storing chlorine are well developed. In 1976, the total production of chlorine in the U.S.A. was about 10 million tons and large quantities were transported safely in trucks, railroad cars and barges; (v) the system will operate at low temperatures ($< 100^\circ C$); (vi) though HCl and chlorine are

corrosive chemicals, their corrosion problems below 100 °C should be much less than those of alkali metals and their salts at temperatures above 400 °C; (vii) all the reactants for chemical and electricity generation are stored outside the cell. Thus, the sizes of the electrochemical conversion devices are relatively small compared to batteries, and scaling up for long duty (weekly) cycles will pose no problems.

The relative merits of the hydrogen-air and the hydrogen-chlorine systems are presented in Table 1. The advantages of electrolysis of HCl, instead of water, are clearly seen. A calculation was made of the material (fuel, oxidant and Fe-Ti) requirements for a 26 MW output energy storage system based on a 10 hour charge/10 hour discharge cycle. Results of these calculations along with similar information for a hydrogen-air system are given in Table 2.

TABLE 1

Comparison of the electrochemically regenerative H₂-O₂ and H₂-Cl₂ energy storage systems — performance, safety and storage aspects.

	H ₂ -O ₂ *	H ₂ -Cl ₂ *
1 Reversible potential (V)	1.23	1.35
2 Projected lowest potential in electrolysis	1.65	1.50
3 Projected highest potential in fuel cell	0.80	1.20
4 Projected highest <i>EFE</i> efficiency (%)	48	80
5 Hazardous chemical produced at cathode	yes	yes
6 Hazardous chemical produced at anode	no	yes
7 Methods now available for handling the hazardous chemicals	yes	yes
8 Materials problems for storage of anode product	yes (if pure O ₂)	yes (but solved)
9 Energy needed for storage of anode product	high for pure O ₂ , low none for air	

* Operating at a current density of 300 - 400 A/ft².

Electrochemically regenerative hydrogen-chlorine cell, system definition and projected performance

A hydrogen-chlorine cell with a solid polymer electrolyte (*e.g.*, Nafion membrane impregnated with catalyst, which is a spin-off from the General Electric fuel cell and water electrolysis cell technology), appears most attractive for an electrochemically regenerative hydrogen-chlorine system. The novel features of this type of cell are: (i) the design of a cell with a solid polymer electrolyte appears to be the most suitable form of cell construction, taking into consideration that there is gas generation during the electrolyzer mode and its utilization in the fuel cell mode; (ii) the solid polymer electrolyte is a highly stable perfluorinated-sulfonic acid ion exchange membrane which is not affected by strong acids and chlorine. It acts as a high conducting

TABLE 2

Comparison of the electrochemically regenerative H_2-O_2 and H_2-Cl_2 26 MW(e) energy storage systems — fuel, oxidant and metal hydride requirements by electric utility

	H_2-O_2	H_2-Cl_2
Total energy stored (MWh)	260	260
Fuel cell voltage (V)	0.80	1.20
Weight of hydrogen stored (lb)	26.7×10^3	17.8×10^3
Weight of metal hydride (MH) required to store above amount of H_2 (lb)	2.3×10^6	1.5×10^6
Weight of Cl_2 stored (lb)	—	0.63×10^3
Weight of MH per kWh (lb)	9.0	6.0
Weight of H_2 per kWh (lb)	0.10	0.07
Weight of Cl_2 per kWh (lb)	—	2.4

electrolyte allowing rapid transport of H^+ ions while the intermixing of gases is prevented; (iii) the device employs porous metal electrodes and low contact resistance bipolar current collectors, thus maintaining a high efficiency to at least 500 amperes per square foot (ASF).

The projected performance of the electrochemically regenerative hydrogen–chlorine cell with today's technology and an advanced one that will be developed in a six year program are shown in Fig. 2. Experimental results, such as those depicted in this Figure, show that even at high current densities (500 ASF), the operating cell potential departs from the reversible value only due to ohmic losses. From the data shown in Fig. 2, it appears that the efficiency for the regenerative hydrogen–chlorine cell should be about 70% at a current density of 300 ASF. By advancing the state-of-the-art, even higher efficiencies are projected at higher current densities.

Economic impact of implementing a hydrogen–chlorine energy storage system

A preliminary estimate of the investment cost in a hydrogen–chlorine electric energy storage plant is shown in Table 3. For the sake of comparison, the projected cost of an advanced technology hydrogen–air energy storage system, as reported in ref. [3] is also shown. The cost figures shown in Table 3 should be regarded as estimates of achievable costs, assuming that vigorous research and development programs will be carried out, and should be used for comparative purposes only. The elimination of the electrolyzer subsystem and the addition of the chlorine storage equipment are found to result in a capital cost reduction for the hydrogen–chlorine system of 24% compared with the investment cost of the hydrogen–air electric storage plant. Owing to the improved conversion efficiency, a smaller sized bed is required for identical storage capacity, so that lower hydride storage costs, compared with ref. [3], are reported here. The chlorine storage costs were obtained from ref.

TABLE 3

Summary of installed cost estimates of a 26 MW(e) hydrogen-air and hydrogen-chlorine electric energy storage plants. All costs are in year 1975, \$/kW(e)

Item	Hydrogen-air ¹		Hydrogen-chlorine ³	
	10 h	10 h	20 h	25 h
1 Water electrolyzer and auxiliaries	140 ⁴	—	—	—
2 Hydride storage subsystem ⁶	170	110	220	275
3 Fuel cell package ⁵	100	90	90	90
4 Chlorine storage subsystem ⁶	—	85	170	212
5 Miscellaneous plant equipment ²	200	165	175	185
Total	610	450	655	762
Plant energy cost (\$/kWh)	61	45	33	31

¹Data from Table 1 from paper by A. Beaufriere, *et al.* [3].

²Includes piping, valve controls and instruments, secondary equipment structures and foundations.

³Cost estimates from ref. [4].

⁴This estimate is based on the power output at the fuel cell end of the complete conversion system.

⁵Power conditioning equipment at \$ 50/kW(e) not included.

⁶Capital cost component increases in direct proportion with the discharge time. This may be an over conservative assumption.

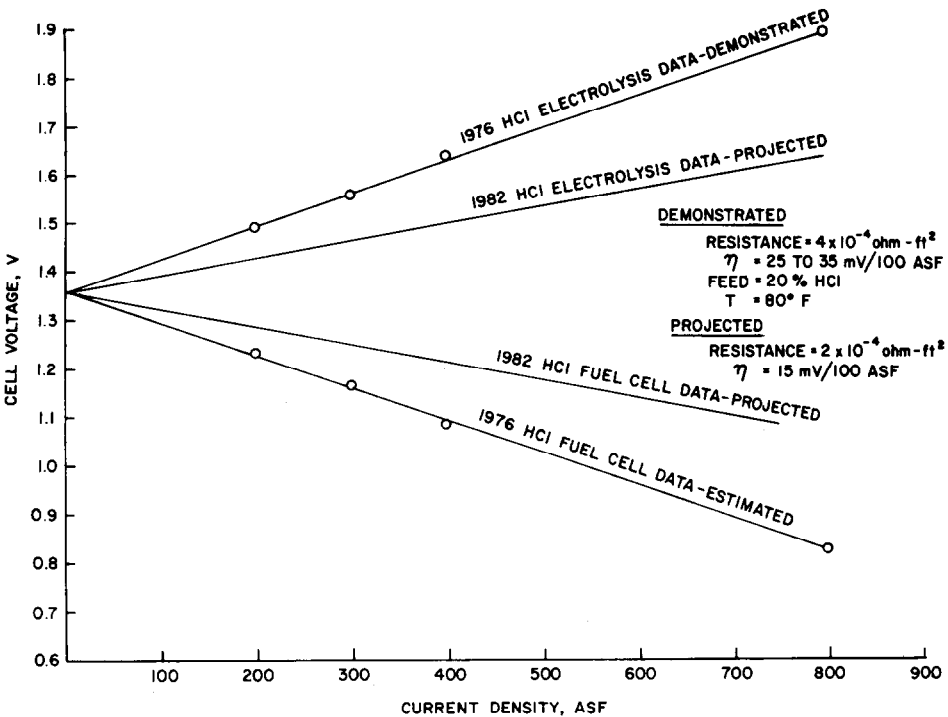


Fig. 2. Demonstrated and projected performance of HCl electrolysis and H₂/Cl₂ fuel cell.

[4] and are within the low but achievable side of the range of existing cost estimates. The miscellaneous plant equipment costs, in the hydrogen-chlorine plant, were reduced by 10% as compared with the corresponding cost item for the hydrogen-air system, to account for the fact that one major subsystem, *i.e.*, the electrolyzer and its associated auxiliaries are not required in the hydrogen-chlorine plant configuration. The fuel cell component of the plant cost was kept unchanged as it is estimated that up to 80% of this cost is relegated to auxiliaries such as converter/inverter which are not affected by the efficiency improvements projected here.

The expected investment costs of the hydrogen-chlorine electric storage plant can be compared with the allowed costs for a generalized "black box" storage plant as computed in ref. [5] and modified for 1975 dollars. These break-even capital costs are shown in Fig. 3, and were computed for electric storage plants, which serve peak load demands and compete with oil-fired power plants and gas turbines for peak load applications. The high distillate oil price of \$ 3.9/10⁶ Btu or \$ 22.7/barrel, which is our estimate for oil prices during the 1985-1990 time period, result in large allowed cost figures for the competing electric storage plants. The National Energy System description and optimization model used to obtain data shown in Fig. 3 are described in refs. [6] and [7]. On inspection of Fig. 3, it is seen that for *ETE* conversion efficiencies of 0.70 to 0.80, break-even costs of \$ 700/kW(e) to \$ 750/kW(e), respectively, are computed. The fact that the allowed costs of the hydrogen-chlorine storage plants shown in Fig. 3 are higher than the expected investment costs as reported in Table 3, indicates that it should be economical to bring these storage plants into the future (year 1985) electric generating mix of the U.S.A. These electric storage plants will be introduced, so as to displace the less economical peaking power plants as fuel cost increases.

We have attempted to compute the annual and unit operating costs of the hydrogen-air and hydrogen-chlorine electric storage plants. These cost estimates include credit for the hydrogen produced for injection into the natural gas pipelines. A similar cost breakdown for gas turbines is also included in the computations. The gas turbine parameters were chosen to represent advanced 1980's technology and include \$ 200/kW(e) capital cost, 11,500 Btu/kWh heat rate and distillate oil price of \$ 3.9/10⁶ Btu. The basic assumptions made in the computations are listed in the footnotes to Table 4. The \$ 6/10⁶ Btu value of the hydrogen credit assumed here, corresponds to the high, but the more realistic, projected synthetic fuel costs according to the Federal Energy Administration's National Energy Outlook, 1976, [8], and it represents about half the projected hydrogen production costs [9, 10]. Had a greater hydrogen credit been assumed here, the economics of the hydrogen energy storage plants, which also produce hydrogen for natural gas supplementation would be improved. The off-peak power available in a weekly cycle is distributed almost half over the weekend and half over the five weekdays (45:55 ratio) [9]. Storage charging will be performed in part during the weekends and in part during the weekdays. Hydrogen production for natural gas supplementation will be performed mostly on weekends, using

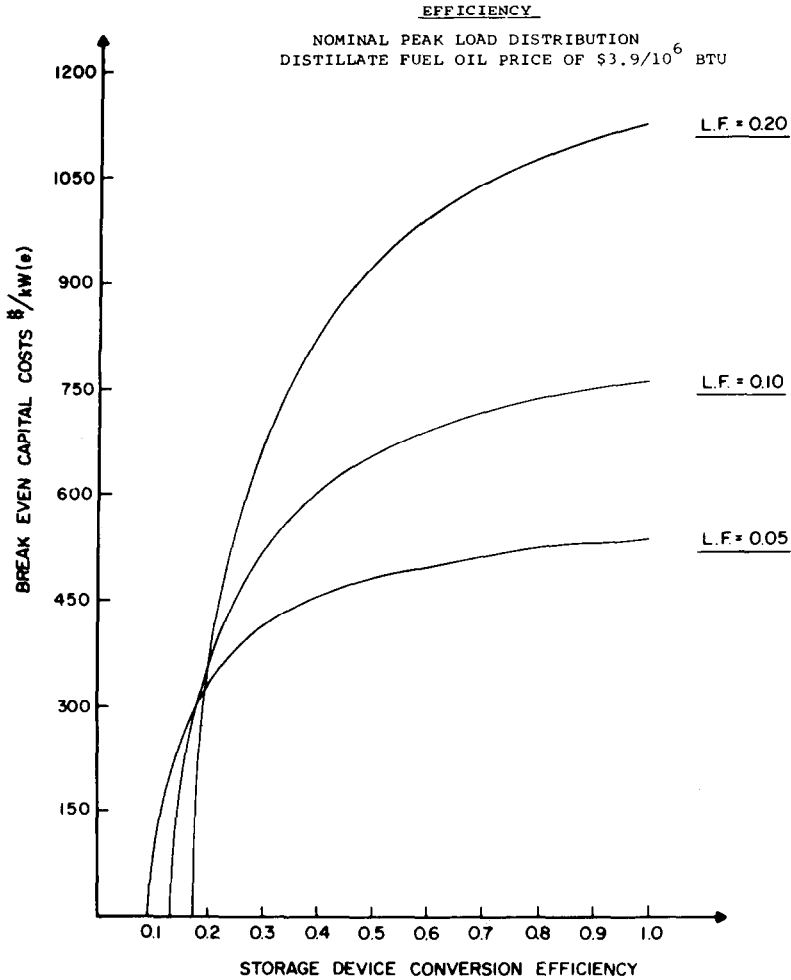


Fig. 3. The break-even capital costs of the "black box" storage device as a function of the conversion efficiency.

that part of the available off-peak power not required for electric storage. This product hydrogen will, in effect, be stored in the natural gas pipeline system. It is assumed here that the hydrogen-chlorine cell will operate in the electric storage and generation modes, while operation in the water electrolysis mode will allow the supply of hydrogen for natural gas supplementation. The computed hydrogen credit is based on the expected hydrogen production rate, assuming a unit hydrogen price of $\$6/10^6$ Btu, as mentioned above. The hydrogen credit is subtracted from the cost of the required off-peak electric power to obtain the net variable production costs.

The results of the annual and unit cost computations are shown in Table 4. It is found that the hydrogen-chlorine system's unit production costs are

TABLE 4

Unit electricity production costs of hydrogen-air and hydrogen-chlorine electric energy storage plants and advanced gas turbines¹

Generating plant	Hydrogen-air		Hydrogen-chlorine		Gas turbine
Weekly operating cycle:					
Daily discharge period (h)	4.0	6.0	6.0	9.0	9.0
Weekly electricity discharge (h) ²	20.0	30.0	30.0	45.0	45.0
Weekly hydrogen production (h)	20.0	0.0	20.0	0.0	0.0
Equivalent electric load factor	0.12	0.18	0.18	0.27	0.27
Equivalent hydrogen production L.F.	0.12	0.00	0.12	0.00	0.00
Required storage capacity (h) ⁶	12.0	32.0	12.0	32.0	0.0
Plant data:					
Capital cost (\$/kW(e))	645	985	490	860	200
Overall conversion efficiency ⁴	0.50	0.50	0.75	0.75	0.30(3)
Unit production costs ⁵ :					
Investment charge (mills/kWh)	92.0	93.7	46.9	54.5	12.7
Electric power input cost (mills/kWh)	31.1	20.0	20.3	13.5	-
Distillate oil cost (mills/kWh)	-	-	-	-	44.9
Hydrogen sales credit (mills/kWh)	-18.4	0.0	-12.0	0.0	-
Net unit variable cost (mills/kWh)	12.7	20.0	8.3	13.5	44.9
Overall unit electricity cost (mills/kWh)	104.7	113.7	55.2	68.0	57.6

¹The following basic assumptions, common to all the three plants considered here, are: 10 MW(e) standard plant size, 30 years lifetimes and an implied capital recovery factor of $CRF = 0.15 \text{ (yr}^{-1}\text{)}$, 10 mills/kWh off-peak power cost, 6 $\$/10^6$ Btu hydrogen credit, 3.9 $\$/10^6$ Btu distillate oil price to gas turbines.

²The following weekly distribution of off-peak power available to the storage plants is assumed: 7 hours each weekday or $7 \times 5 = 35$ h/week, 25 hours over the weekend. Total of $25 + 35 = 60$ hours/week. This figure is averaged from the data of Table 3 - 1, p. 3 - 4 of ref. [11]. It is assumed that all the available weekly off-peak power is utilized for electric energy storage and/or for hydrogen production. The electric power charging requirements are met during the weekdays and in a part of the weekend. The rest of the weekend off-peak power is utilized for hydrogen production. The nine hour daily discharge cycle in the case of the hydrogen-chlorine system and the six hours cycle in the case of the hydrogen-air system correspond to an all-electric operation while the six and four hour daily discharge cycle correspond to operation in the electric and gas sectors.

³Corresponding to a plant-heat rate of 11,500 Btu/kWh.

⁴Overall conversion efficiency of the electric storage plants is the electric to electric conversion ratio. Water electrolysis efficiency for both storage plants is estimated at 0.9.

⁵Operating and maintenance costs estimated as 1 - 3 (mills/kWh) for all the power plants considered here are not included in this comparative evaluation.

⁶The required storage capacity is computed as the sum of the daily charging period (7 hours) and the amount of time during the weekend when hydrogen is produced for electric power generation. The metal hydride and chlorine storage requirements are linearly related to the storage capacity requirements in hours and in turn increase the plant capital cost according to Table 3. The hydrogen produced for sales is assumed to require no storage capacity as it is directly injected to natural gas pipelines or sold to near-by industrial customers.

52-60% of the unit production costs for the hydrogen-air electric storage plant. The cost for the hydrogen-chlorine system is comparable to the cost

of electricity produced by gas turbines and has the obvious advantage that no fossil fuel is required. Possible reduction in capital cost of the storage device, larger credit from the hydrogen production for industrial purposes and the expected improvements in the *ETE* conversion efficiency will make the hydrogen-chlorine system an even more cost effective energy storage system for peak and intermediate load application in the electric utility industry.

Conclusions

The hydrogen-chlorine electric energy storage plant shows a distinctive advantage over the hydrogen-air storage system, both conceptually and economically. The proposed system is flexible in the sense that both the water and hydrochloric acid electrolysis and the hydrogen and chlorine conversion to electricity can be performed within the same cell. This simple system configuration offers the possibility of capital cost reduction coupled with improved conversion efficiency. Should the chlorine handling and storage costs prove to be relatively low, then the hydrogen-chlorine system should compete economically with other proposed storage devices, and with gas turbines, for peak and intermediate load applications in the electric utility industry. The system lends itself to easy scale-up in terms of the total energy stored and, thus, its advantage over rechargeable batteries becomes more pronounced when the storage of off-peak power on a weekly cycle is considered.

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