PREDICTIVE MAINTENANCE OF TITANIUM NOZZLES TO PREVENT CORROSION FAILURES

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The titanium nozzles which feed carbon-dioxide to the urea autoclaves are subject to severe corrosion and may fail as a result. The thickness profile of the corroded and failed nozzles indicate that the corrosion severity is non-uniform along the length of the nozzles, maximum attack being concentrated at about 25 mm from the top end

In the absence of conditions that can cause erosion, the mechanism of corrosion involves repeated invasion of the nozzle by the liquid phase present in the autoclave The kinetics of dissolution, in the liquid phase, of oxygen and hydrogen sulphide (present in the CO_2 feed) determine the location of attack.

Corrosion of the CO_2 nozzles is unavoidable. The only way to prevent failures is through predictive maintenance, aided by rigorous and accurate inspection, which are indicated in the paper.

The urea autoclaves at the Gorakhpur unit of F. C. I. have 4 nozzles each. Of these, three are inlet nozzles, through which ammonia, recycle carbamate (RC) solution and carbon dioxide are introduced into the autoclave. The fourth is an outlet for the urea solution from the autoclave. All the nozzles are of titanium KS 70 (JIS) and experience high temperature and pressure conditions. Fig. 1 shows the location of the nozzles, their dimensions and the approximate operating conditions.

Three types of attack are possible in these autoclave nozzles, viz., erosion, spiralling erosion and corrosion (Fig. 2).

1. **Erosion** : Titanium has a high resistance to erosion. the critical velocity[1] being more than 10 m/sec. The velocity in the inlet nozzles is low ($<$ 2–3 m/sec) and therefore erosion attack is not expected. However erosion is possible at places of change of section where there is a sudden change in velocity. Such locations occur near the top end of the ammonia and RC nozzles. The profile of attack is depicted in Fig. 2 (a). The erosion rates are quite small ($< 0.3 \times 10^{-4}$ mm/hr) and are not expected to result in the failure of the nozzles in a reasonable period (say 100,000 hours of service).

2. **Spiralling Erosion** : This type of attack is encountered in the inlet nozzle of the urea autoclave, where the velocities of flow are high (about 10 m/sec,

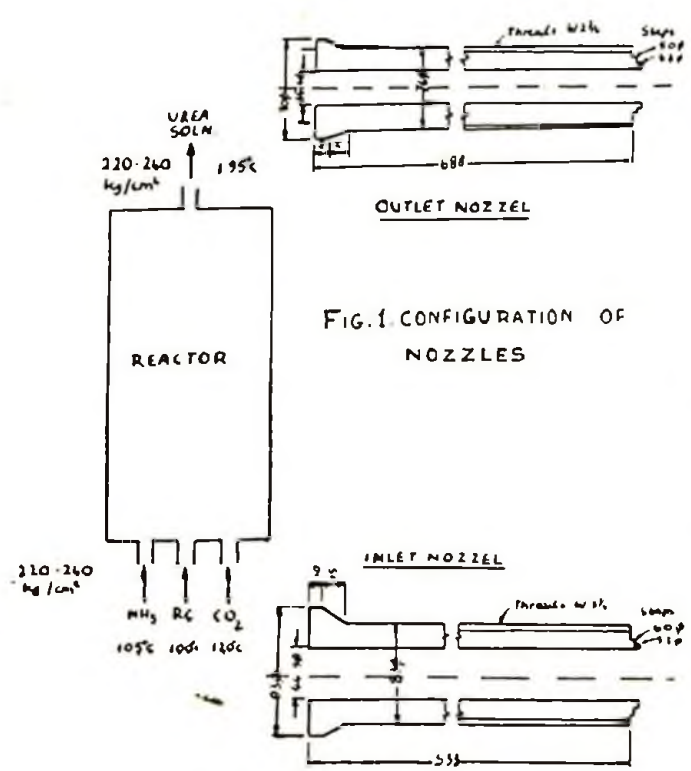


FIG. 1 CONFIGURATION OF NOZZLES

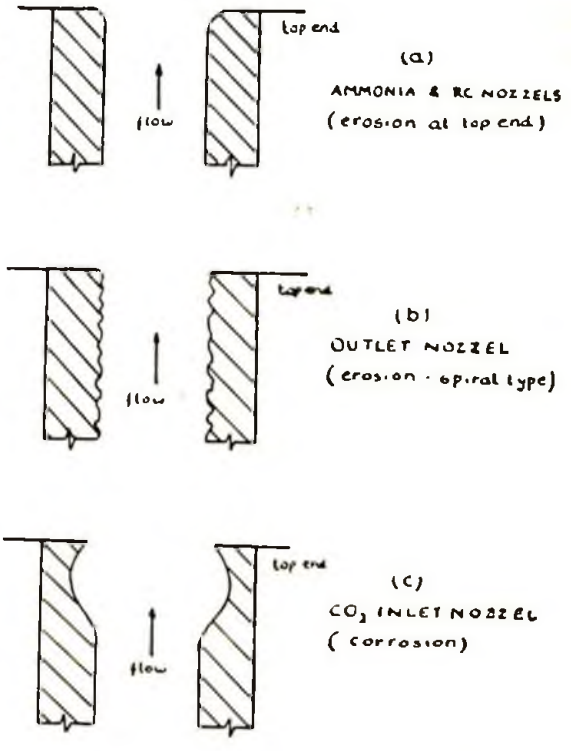


Fig. 1. Configuration of Nozzles.

Fig. 2. Modes of attack in Nozzles.

near the critical velocity for erosion of titanium). Also, since the corrosive urea solution exits suddenly from the autoclave through the outlet nozzles, spiralling motion is to be expected. Both these factors combine to produce spiralling erosion, depicted in Fig. 2 (b). The attack is characterised by spiral grooving all along the length of the nozzle, and occurs at a rate of about 1.0×10^{-4} mm/hr.

3. **Corrosion :** Corrosive attack occurs only near the top end of the CO_2 inlet nozzle. The attack is non-uniform along the length of the nozzle and is maximum at about 25 mm from the top end, being entirely absent at places which are more than 150 mm distant from the top end Fig. 2 (C). While erosion and spiralling erosion effects decrease with the diameter of the nozzle due to the attack, the rate of corrosion remains constant as the diameter increases. Corrosion rates of $2\text{-}5 \times 10^{-4}$ mm/hr are obtained at the region of maximum attack.

OBSERVATIONS AND CASE HISTORY OF A FAILURE

The data on the autoclave nozzles are summarised in Table I. It is immediately evident from the data that the CO_2 inlet nozzle and the outlet nozzles are the ones that deserve maximum attention ; the ammonia and RC nozzles have low rates of attack and are not regions for concern.

The CO_2 inlet nozzle is the most important since (a) the rates of corrosion are high and (b) the maximum corrosion occurs neither at the ends nor uniformly, but at some distance away from the top end. Inspection is thus made difficult and the failure of a CO_2 inlet nozzle occurred due to this factor. The nozzle broke into two. Corrosion had progressed to such an extent that at some regions the wall thickness had reduced to 0.6 mm from an original 19.25 mm. The two broken parts do not match (fig. 3 is the profile of the two broken pieces) signifying that the fracture zone must have shattered into pieces under the high pressure at the time of failure. The fracture had been brittle. (Fig. 4, 5.)

While the top 80 mm of the nozzle exhibited saucer-shaped pits, up to 1 mm deep, such grooving or pitting or any other evidence of corrosion was absent from the lower portion of the nozzle, which was covered by a grayish protective film. Similiar observations were made on the other CO_2 inlet nozzles also.

MECHANISM OF CORROSION IN CO_2 INLET NOZZLES

The possibility of erosion playing any significant role in the corrosion of the CO_2 inlet nozzles can be logically excluded, considering the low velocities of flow (<2-3m/sec). Corrosion would depend on the presence or absence of a protective oxide film on the surface. Titanium surface passivates easily, the thickness of the passive film increasing with time[2]. Only in the presence of a reducing atmosphere, where the film is not self-healing, does corrosion of titanium occur. If a situation is visualised where the liquid phase of the autoclave enters the CO_2 inlet nozzle, the observed corrosion behaviour can be explained.

Such a situation does in fact occur, as a result of the feed design to the autoclaves. Reciprocating machines are used for feeding CO_2, ammonia and RC solution into the autoclaves. The discharge pressure of these machines varies between 230 and 240 kg/cm^2. Since the frequencies at which these feeders operate are different, there is no possibility of synchronizing their

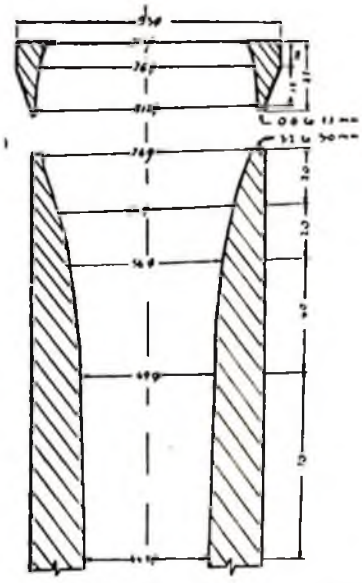


Fig. 3. Profile of Broken Nozzle.

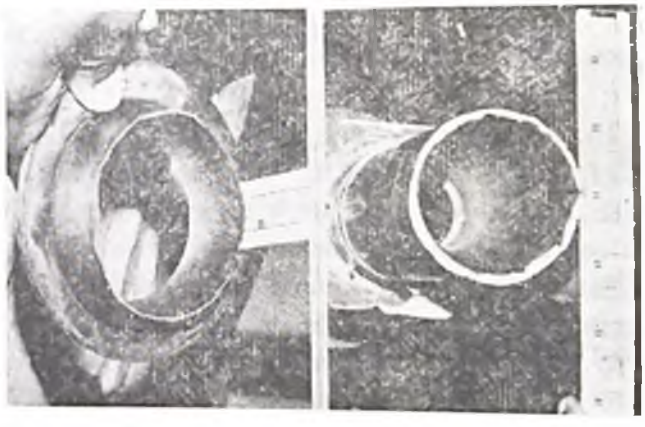


Fig. 4. Photograph of the Top Portion of the Broken Nozzle.

Fig. 5. Photograph of the Bottom Portion of the Broken Nozzle.

discharges. Thus, the CO_2 inlet nozzle may experience a low pressure of 230 kg/cm² at a time when the ammonia and RC inlet nozzles are discharging into the autoclave at 240 kg/cm². Since the nozzles are closely spaced, such a situation could lead to the flow of the liquid phase into the CO_2 inlet nozzle. A schematic picture is presented in Fig. 6. It must be noted that the situation would be different for the ammonia and RC nozzles, because (a) liquid phases have lower compressibilities in general than gaseous phases and (b) unlike CO_2 which would bubble into the liquid phase of the autoclave, ammonia and RC solution mix gradually since no phase change is encountered.

Three regions having different conditions can be identified in Fig. 6 : Region I, fully liquid phase ; Region II, the interphase and Region III, the gas phase. It is obvious that corrosive conditions can be present only in regions I and II. The probable temperature profile is also plotted in Fig. 6. The rate of attack would, as suggested by this temperature profile, increase as the top end of the nozzle is approached.

However, two other factors determine the rate of corrosion. The first is the CO_2/NH_3 ratio. Since. CO_2 is the corroding species (in the liquid phase), the corrosion rate would increase with an increase in the CO_2/NH_3 ratio. There is a gradual decrease in this ratio as the top end of the nozzle is approached due to dilution of CO_2 by the liquid phase and thus the corrosion rate falls towards the top end of the nozzle.

The kinetics of dissolution of oxygen and hydrogen sulphide in the liquid phase also determine the location and rate of corrosive attack. CO_2 injected contains about 800 ppm of oxygen (added intentionally for preserving the passivity of the titanium surface) and about 10 ppm of hydrogen sulphide (usually 3 ppm, but the H_2S content can go up to 10 ppm). Hydrogen sulphide dissolves much faster than oxygen in the liquid phase, as suggested by the solubility figures for the two gases in water (0.810 and 0.500 v/v for hydrogen sulphide and 0.017 and 0.010 v/v for oxygen at 100°C and 200°C respectively[3].) Thus, there is an imbalance in the contents of H_2S and oxygen at the interphase and the oxygen content is insufficient to provide protection in the presence of the reducing effect of H_2S. The protective film is thus eaten away and corrosion, in the form of saucer-shaped pits and shallow grooves, occurs. This mechanism explains why the corrosive attack is localized at about 25 mm from the top end of the CO_2 inlet nozzle.

PREDICTIVE MAINTENANCE SCHEDULE

The chief aim of predictive maintenance is to prevent unnecessary and excessive preventive maintenance by means of on-the-line non-destructive testing methods. In case of the autoclave nozzles, which are enclosed (in the shell of the autoclave) and therefore, inaccessible, on-the-line testing would be impossible. However, characterization of the types of attack and knowledge of the rates of attack make it possible to limit the number of inspections necessary. The need for opening the top cover of the autoclave for inspecting the top end of the CO_2, ammonia and RC nozzles and the bottom end of the outlet nozzle, is eliminated with the help of a specially designed internal recess gage.

From the material properties (UTS for KS 70 is 46 kg/mm²) and the dimensions of the nozzle, the minimum thickness t_{min}, necessary for sustaining an internal pressure of 240 kg/cm² can be calculated as 7.25 mm for the inlet nozzles and 6.15 mm for the outlet nozzle [from $t_{min} = PD/(2S + 2YP)$, where P = internal pressure, D = outer diameter, S = allowable stress = $\frac{1}{4}$ UTS or 5/8 YS, Y = 0.4 for temperature upto 500°C ; [Ref. 4 and 5). It now remains to fix the allowances.

For the outlet nozzle, the seating of the let-down valve placed on top of the autoclave is more important, since if there is a mismatch in the seating, heavy leakage would occur. Thus the outlet nozzle is replaced as soon as the first step provided (at 43 mm, See Fig. 1) is eroded away, and erosion is not allowed to assume any importance. When the nozzle is replaced, it will still have a thickness of 13.65 mm, or about twice the t_{min} as calculated above.

As can be seen from table I, the ammonia and RC nozzles have extremely low erosion rates, even at the top ends. Since the rates of erosion are less than 0.3×10^{-4} mm/hr, there nozzles too will withstand for at least 200,000 hours of operation.

The CO_2 inlet nozzles are a real cause for concern. These nozzles can be considered unsafe if the thickness at any place has reduced to a value less than 7.25 mm. Failure may be considered imminent if the wall thickness reduces to below 5.25 mm, 2 mm lower than t_{min}. To obtain the minimum thickness for absolute safety, a corrosion allowance of 1.65 mm (= 0.065" for pipes with diameter > 1" ; Ref. 6) and an eccentricity allowance of 1 mm are to be added to the value of t_{min}. Thus the safe $t_{min} = 7.25 + 1.65 + 1 \approx 10$ mm.

Data on the corrosion of CO_2 inlet nozzles are plotted in Fig. 7 and it is found that the points lie within a band, the rate of corrosion varyIng between 2.66×10^{-4} and 4.80×10^{-4} mm/hr. The three thickness values already identified are marked off in Fig. 7, to obtain four regions.

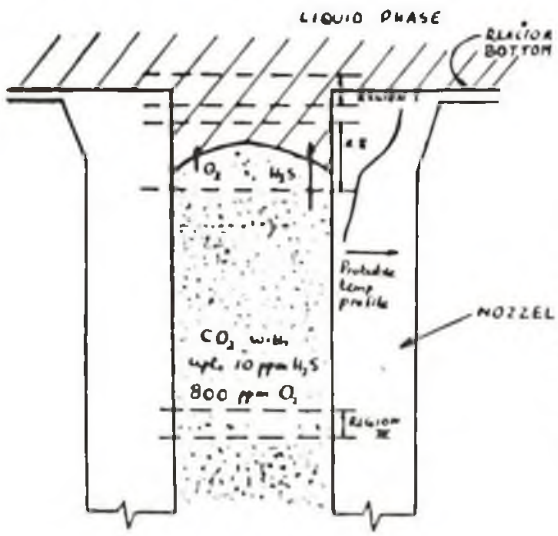


Fig. 6. Probable Mechanism of Corrosion

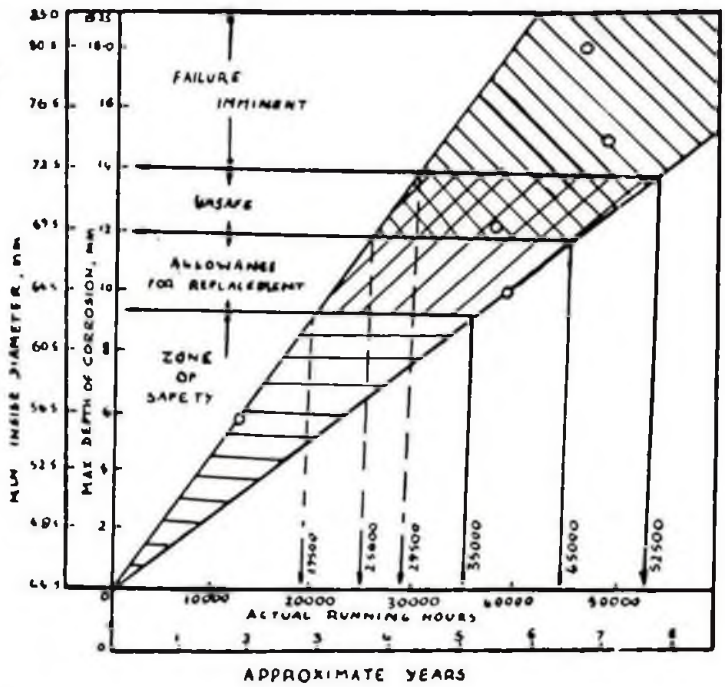


Fig. 7. Predictive Maintenance Schedule

Region	Min. wall thickness mm	Max. Corrosion mm	time, hours min	max.
1. Zone of safety	> 10.0	< 9.25	< 19500	< 35000
2. Allowance for replacement.	7.25-10.0	9.25-12.0	19500	45000
3. Unsafe	5.25-7.25	12.0-14.0	25000	52500
4. Failure imminent	< 5.25	> 14.0	< 29500	> 52500

The predictive maintenance schedules for the autoclave nozzles is thus formulated :

1. Ammonia and RC inlet nozzles :

Type of attack — erosion at top end
Rate of attack — $< 0\ 3 \times 10^{-4}$ mm/hr
Safe operating hours — > 100,000
Inspection — Once in 13000 hrs for max. dia
Replacement — diameter at any point > 63.0 mm within 3000 hrs ; diameter > 67.0 mm immediate.

2. Outlet nozzle :

Type of attack — spiralling erosion
Rate of attack — 1.0×10^{-4} mm/hr
Safe operating hours — 30000
Inspection — (a) once in 13000 hrs for max. dia till dia < 41.0 mm at any point.
(b) once in 3000 hrs after dia > 41.0 mm at any point.
Replacement — Diameter at any point > 48.0 mm or diameter at the top > 41.0 mm, within 3000 hrs.

3. CO_2 inlet nozzle :

Type of attack — Corrosion, localized
Rate of attack — $\sim 3.2 \times 10^{-4}$ mm/hr
Safe operating hours — 19500
Inspection — (a) once in 13000 hrs for max. dia till dia < 60.5 mm.
(b) once in 3000 hrs if dia > 60.5 mm
Replacement — diameter at any point > 63.0 mm, with in 3000 hrs ; diameter < 67.0 mm, immediate.

The lining of the urea autoclaves which is made of welded titanium sheets is another area of concern at the Gorakhpur Unit. The lining has leaked 15 times (in 5 autoclaves), each occasion involving an average down time of 1175 hours (equivalent to 7350 tons of urea).

One of the autoclaves has been our siek baby, having leaked 9 times since 1968. These leakages, which are due to pin holes and cracks in the titanium liner, almost invariably occur at or near welded joints. This observation leads us to believe that the passivation film on titanium is dependent on the internal stresses and the repassivation kinetics are slower near the welded joints where thermal stresses have been introduced during fabrication. A thorough analysis is being made of this problem.

The inlet nozzles have similar dimensions and are interchangeable. The interchange involves major piping modifications, but prevents the need for replacing the nozzles. A scheduled interchange, where each nozzle operates as inlet for ammonia, RC solution and CO_2 for 13000 hours each will give an overall safe nozzle life of about 100 000 hours. Such an interchange has been effected in one of the autoclaves after 12300 operating hours and the CO_2 inlet nozzle, which had lost 5.90 mm of the wall thickness due to corrosion is now working as the ammonia nozzle. A similar programme for the other autoclaves is being worked out.

SUMMARY AND CONCLUSIONS

Three types of attacks are possible in the titanium nozzles of urea autoclaves. The corrosive attack on the CO_2 inlet nozzle is the most dangerous because it occurs not at the ends but somewhere inside the nozzle, the mechanism involving entry of the liquid phase into the nozzle. On the basis of data collected, prediction of the life of these nozzles is possible. The formulation of a productive maintenance schedule will result in minimising loss of production due to (i) accidents (ii) Faster replacements than necessary (involving down time of the autoclave) and (iii) running the autoclaves under reduced loads because of the fear of a nozzle failure.

In addition, the predictive maintenance programme will eliminate uncertainty regarding the safety of nozzles and personnel working nearby when the nozzles are suspect, thus avoiding loss of productivity due to the following non-quantisable factors : (i) locking up the time of safety personnel (ii) loss of efficiency of work and (iii) anxiety, leading to inferior quality of work

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Table I Data on attack in Titanium Nozzles.

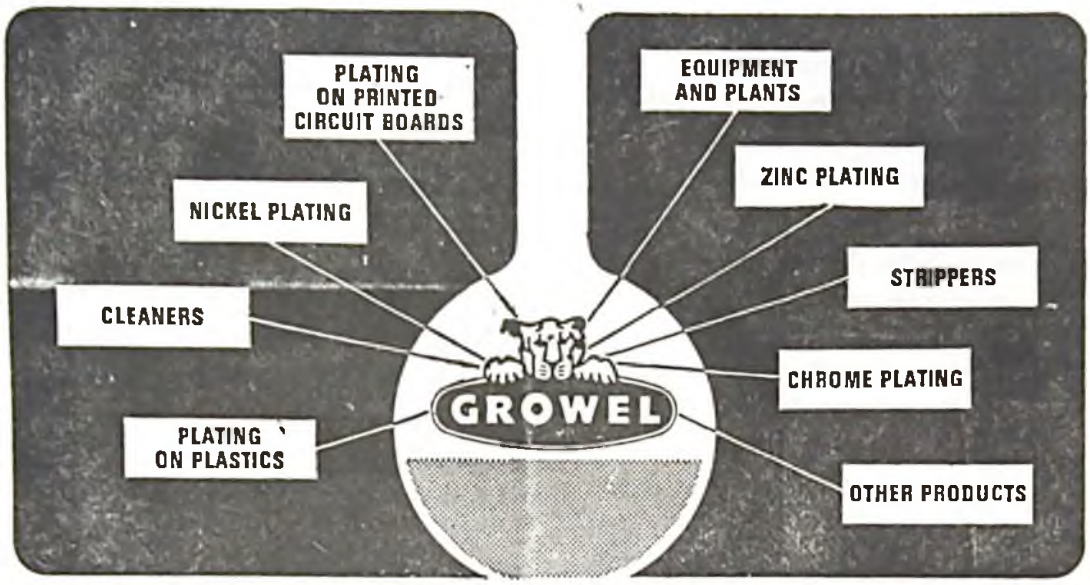
Type of nozzle.	No. of hours.	Max. dia, mm.	Max. Corrosion/erosion mm	rate of attack mm/hr	remarks
Outlet	12500	no evidence of any erosion attack			
	14000	37.5	0.95	0.68×10^{-4}	Max. erosion occurred inside. though the attack was uniform to within 1.5 mm deep grooving characterised the attack.
	19000	39.5	1.95	1.02×10^{-4}	
	35000	43.0	43.60	1.02×10^{-4}	
Ammonia Inlet	24000	45.50	0.50	0.21×10^{-4}	Max. erosion occurred at the entry into the auto clave.
	38000	45.26	0.38	0.10×10^{-4}	
	48770	47.50	1.50	0.31×10^{-4}	
RC soln. Inlet	24000	45.64	0.57	0.24×10^{-4}	Attack only at the entry into the autoclave.
CO_2 Inlet	12300	—	5.90	4.80×10^{-4}	Max. attack occurred between 20 and 30 mm from top end. Shallow pits and grooves characterised the attack
	37567	69.0	12.25	3.26×10^{-4}	
	38497	65.0	10.25	2.66×10^{-4}	
	46800	81.2	18.35	3.92×10^{-4}	
	48770	75.0	15.25	3.13×10^{-4}	

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