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A Study on the Chemical Treatment of Spent Nuclear Fuel

Kim Young Eak

Reactor Engineering Division in Korea Atomic Energy Research Institute

Abstract

A decladding study was performed as the first step in the reprocessing of spent nuclear fuel. In the chlorination expriments, aluminum or Zircaloy-4 which is a common fuel coating material was used as raw material, activated alumina was used as fluidized bed material and the pure nitrogen was used as a dilution gas. The temperature ranges applied in both cases of using Zircaloy-4 were 280-550°C and 350-550°C, respectively. As a result of a measurement of the reaction rate constants it was confirmed that the reaction rate was controlled by surface concentration.

초 록

사용한 핵연료를 재사용 하기위한 재처리의 첫단계인 decladding에 대한 연구를 alumina를 bed material로 사용한 fluidized-bed에서 핵연료 피복재로 많이 쓰이는 aluminum 또는 Zircaloy-4를 원료로 취하여 이에 대한 Chlorination을 실험했다. 희석개스로는 N_2 개스를 사용했으며 온도범위는 Al 원료의 경우는 280-550°C, Zircaloy-4 원료의 경우는 350-550°C이다. 실험결과, 온도 및 시간의 변화에 따른 반응속도 상수를 구했으며, 반응속도는 surface reaction Kinetics에 의해서 재배됨을 알았다.

1. Introduction

The difference between the nuclear fuel and the other forms of fuel is not only its generation of enormous energy from small volume but also the adaptability for recovering nuclear fuel from the spent nuclear fuel.

The recovered fuel can further be used after suitable processnig. Thereupon, the familiar term"Cycle" is often used for the nuclear fuel. The spent nuclear fuel should meet a chemical reprocessing stage in which uranium and plutonium are recovered.

After burning up the enriched (3.38 w/o) uranium in the reactor core of Kori Nuclear Power Plant, for example, it becomes the less enriched one (1.03 w/o) and the weight is also decreased from 16,000 kg to 15,330 kg. The typical fuel cycle applicable to the reprocessing of spent fuel is as shown in Fig. 1[1].

As Fig. 1 shows, the reporcessing is very important process in the fuel cycle. The outline of fuel repro-

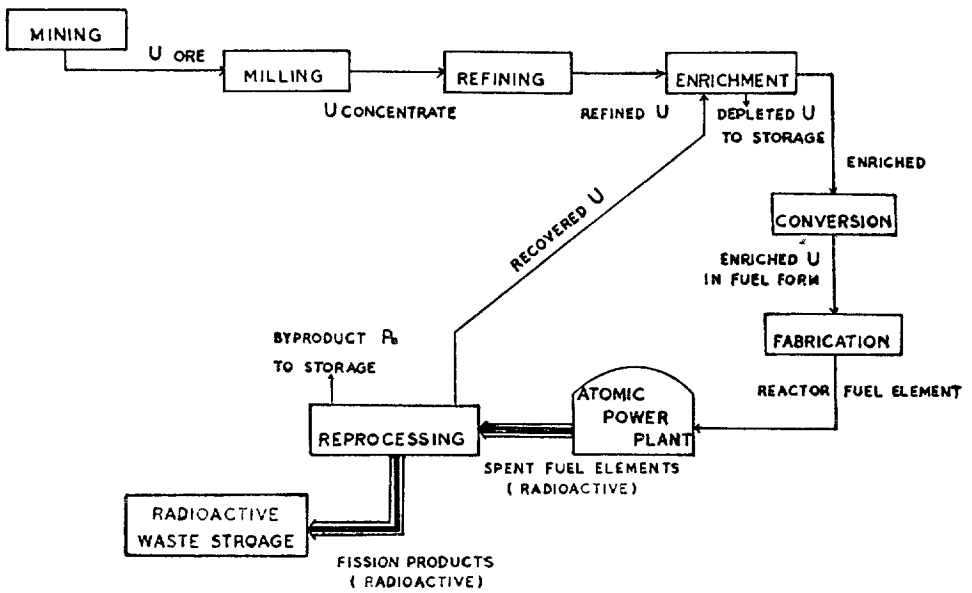


Fig. 1 Schematic Diagram of Nuclear Fuel Cycle

cessing is as follows;[2]

a) Decladding
b) Dissolution
c) Head-and treatment and feed adjustment
d) Extraction and decontamination
e) Partition
f) Stripping and refining
g) Auxiliary processes

Decladding process which plays a key role in the first stage of reprocessing is two kinds; i. e.,

(a) aqueous and (b) non-aqueous (or volatility) process.

The former has been practicaly applied up-to-date, while the latter is still under development stage.

However, the lattter has some advantages;[3] i. e.,

a) Less amounts of radioactive waste are formed.
b) Manipulation is comparatively easy.
c) No conversion is required since the final product, UF_6, is in a gaseous phase.

There are two chemical reaction steps on non-aqueous process;[4]

a) Chlorination step
b) Fluorination step

As a first stage of the succeeding study on the fuel reprocessing, the authors have studied the chlorination method in this paper, using pyrex glass column of which I. D. is 3 cm and the height is 80 cm.

2—1 Theoretical

Aluminum in dluidized bedat 280-550°C reacts with Chlorine to form aluminum trichloride, and the Zircaloy-4 at 350-550°C also reacts with chlorine to form Zirconium tetrachoride.

Such chlorination reactions are thermodynamically exothermic; i. e., the heat of formation of $AlCl_3$ at 298°K and that of $ZrCl_4$ at the same temperature are 328 Kcal/mole and 201 Kcal/mole, respectively.

$$2\,Al\,(s) + 3\,Cl_2\,(g) \rightarrow 2\,AlCl_3\,(g) \qquad (1)$$
$$H_{298} = -328\ \text{Kcal/mole}$$

$$Zr\,(s) + 2\,Cl_2\,(g) \rightarrow Zr\,Cl_4\,(g) \qquad (2)$$
$$H_{298} = -201\ \text{Kcal/mole}$$

The gases of $AlCl_3$ or $ZrCl_4$ are sent to hydrolysis reactor and be hydrolyzed.

$$2\,AlCl_3\,(g) + 3\,H_2O \rightarrow Al_2O_3\,(s) + 6\,HCl \qquad (1)$$

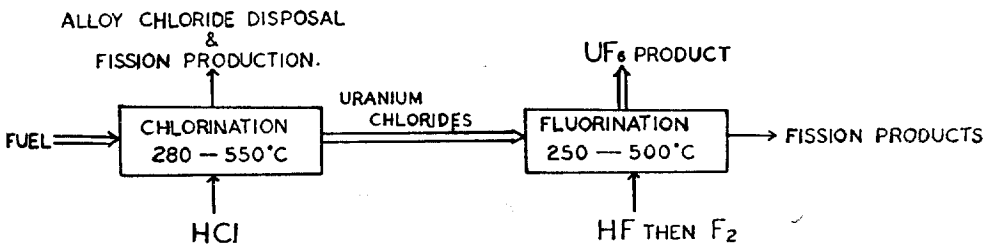


Fig. 2 Volatility Flowsheet for Reprocessing Olloy Fuels

$$ZrCl_4\,(g) + 2\,H_2O \rightarrow Zr\,O_2\,(g) + 4\,HCl \qquad (1)$$

Uranium reacts with chlorine to form mostly solid uranium trichloride and small amounts of solid uranium tetrachloride, and remain in bed together with alumina which is a bed material.

$$U\,(s) + \frac{3}{2}\,Cl_2\,(g) \rightarrow UCl_3\,(s)$$

$$H_{298} = -212\ \text{Kcal/mole}$$

$$UCl_3\,(s) + \frac{1}{2}Cl_2\,(g) \rightarrow UCl_4\,(s)$$

$$H_{298} = -39.9\ \text{Kcal/mole}$$

The chlorination reactions of Aluminum and Zircaloy-4 are further considered as typical heterogenous reactions. Consequently, it may be said that the reaction rates are dependent only on the surface concentration of the reactants in certain definite concentrations. It may be further said that the concentrations of the reactants are as same as the total surface concetrrations. The general heterogenous reaction of solid and gas system can be expressed as follows;

$$A\,(\text{fluid}) + bB\,(\text{solid}) - C \begin{cases} \text{Fluid products} \\ \text{Solid} \quad \text{"} \\ \text{Fluid and Solid products} \end{cases}$$

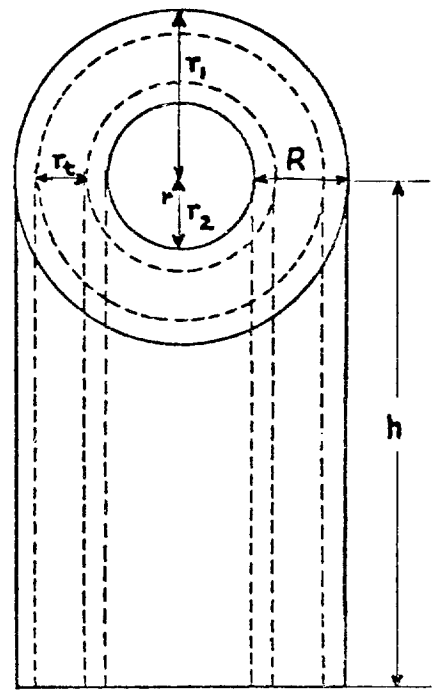
where b: stoichiometric constant

If the unreacted core model proposed by Levenspiel[5] comes into existence, following rate equations are to be derived for column of which height is h (Fig. 3).

$$-\frac{1}{Sex}\ \frac{dNB}{dt} = b\,K_s C_{Ag}$$

$$-\frac{1}{Sex}\ \frac{dNB}{dt} = \rho \frac{dr_c}{B\,dt}$$

Where R: the radius (=thickness of cladding)



Surface Area

$= 2\pi\,(r_1^2 - r_2^2) + 2\pi\,r_1 h + 2\pi\,r_2 h$

Fig. 3 Shape of Sample

before the reaction

r_c: the radius (=thickness of cladding) of the unreacted after reaction.

Therefore, $-\rho_B \frac{dr_c}{dt}$ may be equal to $b\,K_s\,C_{Ag}$

$$-\rho_B \frac{dr_c}{dt} = b\,K_s\,C_{Ag}$$

integrating the above

$$-\rho_B \int_R^{r_c} dx = b\,K_s\,C_{Ag} \int_0^t dt$$

Therefore, $t = \frac{\rho_B}{b\,K_s\,C_{Ag}}\ (R - r_c)$

For reaction (1) $t=\frac{\rho_B}{\frac{2}{3}K_s C_{A_g}}(R-r_c)$

and for reaction (2) $t=\frac{\rho_B}{\frac{1}{2}K_s C_{A_g}}(R-r_c)$

According to the above equations, the ratio of r_c/R is plotted against t, and nearly streight line was obtained [6].

It strongly suggests that the reaction rate is dependent mainly on the surface concentrations.

2-2 Experimental

A) Fuel Charge

In this experiment, the cladding material (Al or Zircaloy-4) together with UO_2 pellets was used instead of using real fuel. Aluminium tubes (I. D. 0. 7 cm, O. D. 0. 9 cm, length 5 cm) of more then 96 % purity which was confirmed by gravimetric analysis were used.

The applied Zircaloy-4 was obtained from SAND VIK, Sweden, and the size of the canning tube was I. D. 0. 9459 cm. O. D. 1. 0744 cm and length 319. 5574 cm. The main component of the Zircaloy-4 tube is Zirconium. Some other slight amounts of metals such as Sn, Fe, and Cr etc. were contained. The used UO_2 pellets were depleted ones and the mean contents of U^{235} is 0. 2 % by weight. The density of the pellets is 10. 36 g/cm^3 which deserves of 95 % of the theoretical density.

B) Alumina Charge

The used alumina as a bed material was chromatograpycal grade and its size distribution is shown in Table. 1. Prior to use the alumina it was heated at 300°C for 3 hers. by activatin.

The pretreated alumina was charged to 10 cm height in the column.

Alumina was found to be a suitable inert bed material since it was not congealed to cake state during or after the reactions[7]

C) Temperature

The temperature was maintained to 280-550°C in case of aluminum as bed material and to 350-550°C in case of Zircaloy-4 as bed material.

Such temperature ranges were chosen condidering the sublimation points of the materials;i. e., the sublimation point of $AlCl_3$ is 180°C at 1 atm and that of $ZrCl_4$ is 331°C at 1 atm. The melting points of UCl_3 and UCl_4 at 1 atm are 840°C and 590°C, respectively.

Table 1. Particle Size Distribution of Alumina

Mesh	Size	Percentage
	+30	1
−30	+40	23
−40	+50	47
−50	+60	16
−60	+120	13

At such temperatures ranges, $AlCl_3$ and $ZrCl_4$ are able to vaporize, and UCl_3 and UCl_4 are to be remained with solid state in the reaction apparatus.

Consequently, the applied temperature ranges are quite suitable as the experimental conditions[8].

D) Reaction Conditions[8]

Concentraction of Cl_2: 0-80 % by volume

Quantity of Cl_2 in case of using aluminum: 1. 5 stolchiometric amount.

Quantity of Cl_2 in case of using Zircaloy-4: 2 stoichimetric amount.

Cas flow rate: 15. 24—21. 34 cm/sec in the fluid Reaction time: 5 hrs per charge.

2-3 Equipment and procedure

A Purex column (I. D. 3 cm, height 80 cm) was used as reaction apparatus (Fig. 4)

The pyrex column was inserted in another Pyrex tubing of which I. D. is 5 cm. The other side tubing was wrapped with asbestoes ribbon and Ni-Cr wire (500 w) was wound on it. By connecting the Ni-Cr wire to electrical source and by heating the other side tubing it was possible to maintain the column at constant temperature.

Rapid cooling of the column was also possible by way of air flowing through the space between the outer side tubing and the column. The size of the

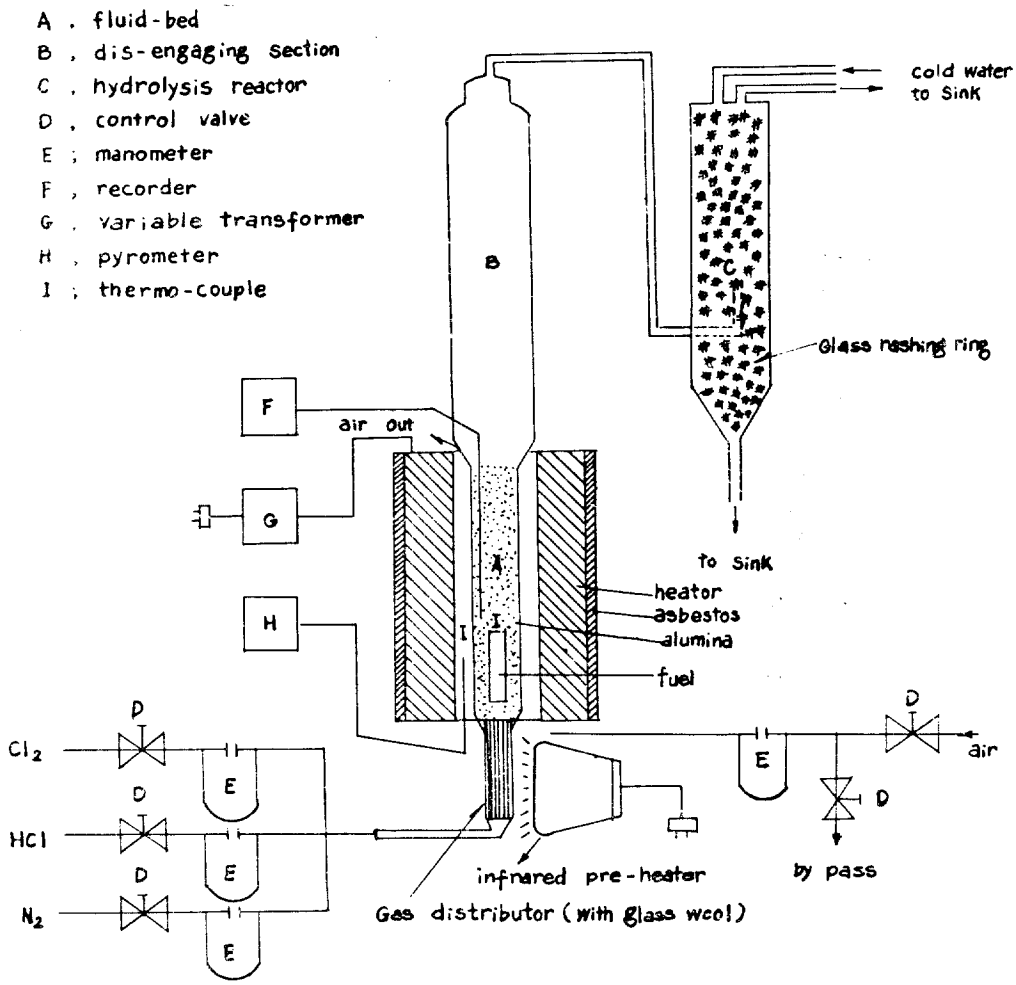


Fig. 4 Schematic Diagram of an Apparatus

disengaging section of the colum was 5 cm in I. D. and 40 cm in height.

Temperature measurements were carried out by inserting thermocouple in the reaction apparatus.

Reactant gas (Cl_2) and diluent gas (N_2) were preheated by 250 w I. R. lamp by passing them through preheating zone prior to be introduced into the reaction apparatus through distributor made of gass wool. Nitrogen gas was used throughout this experiment for the purpose of dilution, purge, and fluidizing the reactant gas. Also, the gases were always flowed through precise orifice mater. The gas evolved in the reaction were sent to hydrolysis reactor. The hydrolysis reactor was made of pyrex column of which I. D. is 5 cm and height is 40 cm. The inner side of the column was charged with glass rasching rings to get efficient contact. By flowing water from the top of the column the gases (mainly $AlCl_3$, $ZrCl_4$ or unreacted reactant gases) formed in the reaction were hydrolyzed and subsequently measured by checking the weight decreased.

The optimum concentrations. temperature and time for the chlorination reactions were measured as well as the dependences of radius on time. Further, the reaction constants were also measured varying reaction temperature.

3. Conclusions and discussion

During or after reactions the bed material, alumina, regardless the type of alumina (i. e., neutral or basic), was not congealed to cake state and kept its free flowing state excellently[7]. The values of the Cl_2 Utilization efficiency are shown in Fig. 5. The maximum observed value of the efficiency was 60 % in both cases of using aluminum and Zircaloy-4. The concentrations of gases versus the extents of reaction of aluminum or Zircaloy-4 are shown in Fig. 6.

In general, the extents of reaction are increased with the concentrations, however, when the extent is above 80%, the increasing rate becomes slight. Therefore, it is desirable to keep the concentration of chlorine gas at 80%. The reaction time (Run duration) versus the extents of reaction of aluminum or Zircaloy-4 are shown in Fig. 7. The extents of reaction are increased with reaction time at the initial stage. of 50 min. But it shows the reaction rate is not much varied Therefore, in this study, the suthors adopted the reaction time of 180 min.

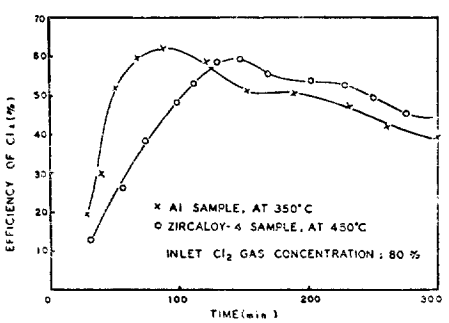


Fig. 5 Cl_2 Utilization Efficiency as A Function of Time

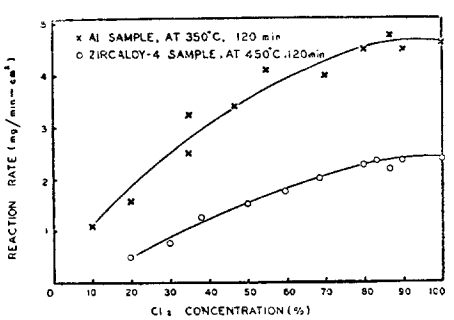


Fig. 6 Reaction Rate as A Function of Concentraation

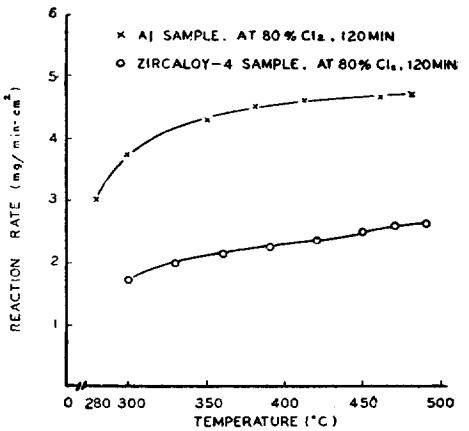


Fig. 7 Reaction Rate as A Function of Time

As fig. 8 shows, the plot of reaction time (run duration) to the ratio of radius (r_c/R) is nearly streight line[6]. The extents of reactions as a function of reaction temperature are shown in Fig. 9 and Fig. 10. The extents of reactions are independent upon temperature in the ranges of 280-550°C for aluminum-and 350-550°C for Zircaloy-4, respectively. Therefore, the authores had adopted the reaction temperatures of 350°C for the reaction of aluminum and 450°C for that of Zircaloy-4. When the reaction rates were plotted as a function of temperature, a sharply increasing parabola was obtained. It means that the reactions are dependent on the chemical reaction controlling[9].

Further, the reaction characteristics of aluminum and Zircaloy-4 are similar in all runs.

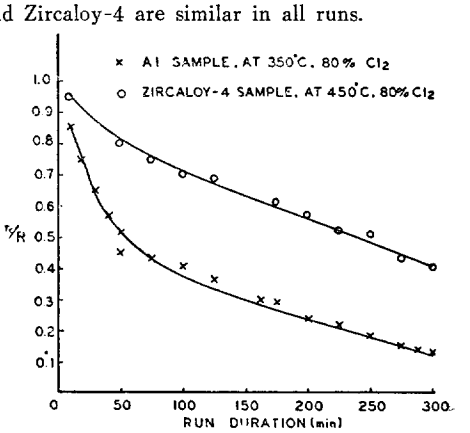


Fig. 8 Change of Radius vs. Time

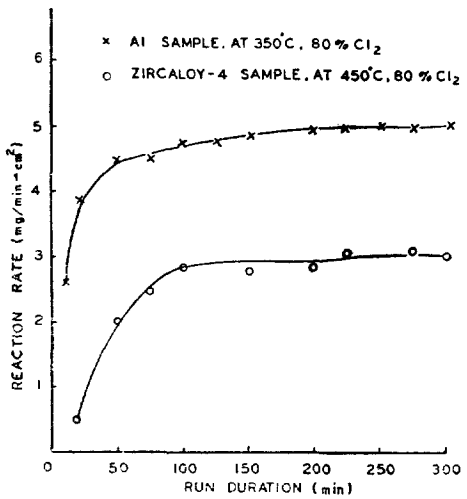


Fig. 9 Reaction Rate as A Function of Temperature

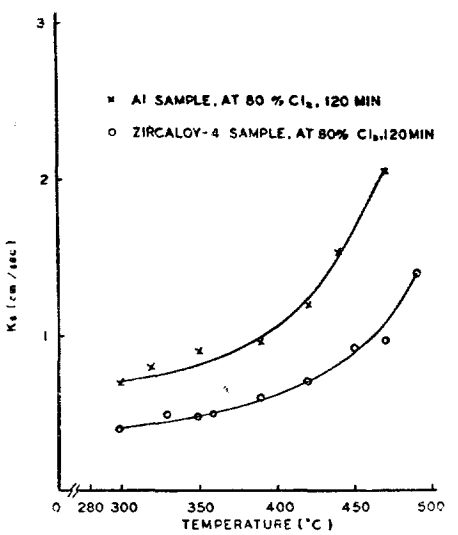


Fig. 10 Reaction Rate Constants as A Function of Temperature

Since these reactions are exothermic, the reactions were able to be controlled by maintaining the bed temperature constant. The maximum fuel temperature was 700°C for U-Zr fuel and 570°C for U-Al fuel. Both are well below the melting points of the respective fuels.

The superficial fluidization velocity was 0.4-0.6 ft/sec.

Nomenclature

A: fluid reactant

b: stoichiometric constant

B: solid reactant c:product

C_{Ag}: concentration of A in gas stream (moles/cc)

K_s: reaction rate constant based on unit surface (cm/sec)

N_A: moles of A

N_B: moles of B

R: radius of particle (cm)

r_c: radius of unreacted core (cm)

S_{ex}: exterior surface of particle (cm^2)

t: time (sec)

V: volume

ρ_B: density of B (mole/cc)

ΔH: standard heat of reaction

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