The Passivation Effects of Magnesium Ion on PHWR Primary Heat Transfer System Structural Materials

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Zinc ion injection passivation technique is being used in BWRs in order to reduce the radiation field build-up around the reactor coolant system. In the case of PWRs and PHWRs, the chemistry of the primary coolant system and the materials of construction are different from those of BWRs. In the present paper, the results of studies on the effect of magnesium ion in modifying the oxide layers formed under PHWR chemistry conditions are reported. The experiments carried out at room temperature and at 265°C are described. Electron spectroscopy for chemical analysis (ESCA) of the materials autoclaved at 265°C in magnesium containing solution has also been reported.

KEYWORDS: PWR type reactors, PHWR type reactors, radiation field, magnesium ions, magnetite film, passivation, corrosion protection reactor materials, primary heat transport, structural materials, ZIP, electron spectroscopy for chemical analysis, depth

I. INTRODUCTION

The two major radioactive isotopes which are responsible for the radiation field build-up around the primary heat transport (PHT) systems of water cooled nuclear reactors are 58Co and 60Co. When the corrosion products are transported to the reactor core, they are activated and deposited on out-of-core surfaces. This causes occupational exposure during maintenance work. Attempts are being made, all over the world, to reduce the activity build-up on the out-of-core surfaces in line with the norms of ALARA. It was discovered that the presence of ppb levels of zinc in the reactor coolant water of some of the BWRs resulted in considerable reduction in the radiation fields. It further led to the adoption of zinc ion injection passivation technique for radiation field control in this type of reactors. Zinc ion at concentrations of 5 - 15 ppb could reduce the activity build-up to a significant extent in the coolant circuits of BWRs which are operated under neutral water chemistry conditions1). The beneficial effects of zinc ion under the simulated primary heat transport system conditions of PWRs and PHWRs have also been reported2). But till today there is no plant experience of using zinc ion as a passivator in either PWRs or PHWRs. In PWRs and PHWRs, the primary coolant is maintained under alkaline conditions and in PHWRs the major construction material is carbon steel. In view of the above differences in the water chemistry and the materials of construction, detailed investigation of zinc and similar ions which have the potential to reduce the activity build-up in PWRs and PHWRs are considered essential.

The two possible mechanisms proposed for the observed reduction in radiation field build-up in BWRs in the presence of zinc are: (i) The zinc ion helps to form a thinner and tenacious oxide layer on the metal surfaces3). This helps to reduce the release of corrosion products to the coolant which in turn results in reduced source term for contamination. Thinner layer holds less inventory of metal oxide and hence radioactivity as well. Both the formation and release rates of corrosion products are reduced significantly. (ii) Zinc ion concentration (15 ppb) being more than 100 times higher than that of cobalt ion (100 ppt), the former can easily compete with the latter for exchange sites on magnetite layer and thereby pre-empt the adsorption of cobalt on magnetite surface.

Zinc ion, though successful in reducing the radiation field build-up in BWRs, the formation of active isotope 65Zn by neutron activation leads to problems of radioactive waste management apart from partially offsetting the gain in the radiation field4). It is quite probable that some other ions, with similar beneficial effects like zinc in controlling the radiation field build up, may exist. Thus, an investigation was carried out to ascertain whether magnesium ion has any such beneficial effects especially under the chemistry conditions prevailing in

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It is well known that zinc and magnesium have similar properties by virtue of their position in the periodic table. Similar electronic configuration, similarity in the sizes of the Zn\(^{2+}\) and Mg\(^{2+}\) ions, and the tendency to form ferrites are the important properties. Table 1 lists the similarities between Zn\(^{2+}\) and Mg\(^{2+}\).

<table>
<thead>
<tr>
<th>Properties</th>
<th>Zn</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic configuration</td>
<td>3d(^{10})4s(^{2})</td>
<td>2s(^{2})2p(^{6})3s(^{2})</td>
</tr>
<tr>
<td>Oxidation state</td>
<td>+2</td>
<td>+2</td>
</tr>
<tr>
<td>Ionic radius (Å)</td>
<td>0.69</td>
<td>0.65</td>
</tr>
<tr>
<td>Ferrites formed</td>
<td>ZnFe(_2)O(_4)</td>
<td>MgFe(_2)O(_4)</td>
</tr>
</tbody>
</table>

Detailed experiments were carried out at 265°C and at pH\(_{25\degree C}\) 10 to investigate the effect of magnesium ion on the formation of oxide film on surfaces of materials such as carbon steel (CS), SUS-304, Incoloy-800, and Monel-400. Room temperature experiments have also been carried out on magnetite powder as well as magnetite coated carbon steel coupons to get the basic information regarding adsorption of Mg\(^{2+}\) and Co\(^{2+}\) ions over magnetite surface. The room temperature studies can also provide some idea about the activity pick-up behaviour in low temperature circuits present in the primary heat transport systems.

II. EXPERIMENTAL

1. Preparation of Oxide Coated Coupons

Coupons of different structural materials viz. carbon steel, SUS-304, Incoloy-800, and Monel-400 of size 30×15×1 mm were prepared. These were polished up to diamond grade and autoclaved at 265°C (the average temperature of PHWR primary coolant) for 7 days in a solution of LiOH at pH 10 (pH measured at room temperature ~25°C). The solution in the autoclave was deaerated by purging with argon gas before heating. 25 ppm of hydrazine was also added to take care of the remaining oxygen. Several sets of coupons were autoclaved to see the reproducibility of the results.

2. Measurement of Oxide Thickness

Thickness of the oxide layer on carbon steel surface, formed both in the absence and presence of Mg\(^{2+}\) ions, was computed from weight loss observed after descaling the oxide coated coupons using Clarke’s solution consisting of 5 g SnCl\(_2\), 2 g Sb\(_2\)O\(_3\) in 100 ml concentrated hydrochloric acid. Necessary corrections for the base metal removed during the oxide film dissolution by Clarke’s solution was applied. Relative thickness of the oxide formed over Incoloy-800 was determined by electron spectroscopy for chemical analysis (ESCA) from the depth profile of oxygen.

3. SEM Examination

Morphology of the oxide formed on the various structural materials were examined using Scanning Electron Microscopy (SEM).

4. Oxide Characterization using ESCA

Oxide characterization of the coupons of the materials Incoloy-800, SUS-304 and Monel-400 were carried out by ESCA. Coupons of size 10×10×1 mm, which were autoclaved both in the presence and absence of Mg\(^{2+}\) ions, were used for the ESCA analysis. VG Scientific (UK) ESCA LAB 200 X with aluminium K\(_\alpha\) X-ray having photon energy of 1,486.6 eV as the probe was used. Depth profiling of the constituent elements in the oxide layer was carried out by repeated etching of the surface to a desired duration with a scanning argon ion beam and analyzing the etched surface after each level of etching. The surface was etched for 300 s at a beam current of 2 μA which corresponds to etching of approximately 10 Å per level. Oxygen concentration profile as a function of depth was used for the measurement of thickness of the oxide layer formed on Incoloy-800. Concentration profiles of different elements were used for the characterization of the oxide.

5. Corrosion Experiment at High Temperature

(1) Conditioning the Autoclave with Mg\(^{2+}\) Ions

The surface area of the autoclave was very large as compared to the surface area of the coupons. Hence, it was felt necessary to saturate the autoclave inside surface coming in contact with the solution with magnesium ion. The autoclave was loaded with a solution containing 100 ppb Mg\(^{2+}\) as (Mg(OH)\(_2\)) at pH 10 and was kept for 2-3 days at high temperature and pressure. The solutions in the autoclave before and after autoclaving, were analyzed for magnesium using Atomic Absorption Spectrometer (AAS) in flame absorption mode at 285.2 nm. This was repeated till the concentration of magnesium in the solution after autoclaving reached the value of 100 ppb.

(2) Corrosion Experiment

Polished coupons of the above mentioned materials were autoclaved at 265°C for 7 days in a solution of 100 ppb magnesium adjusted to pH 10 (LiOH). The autoclave was inerted before raising the temperature. The coupons were removed from the autoclave after 7 days of exposure, and washed thoroughly with demineralized water and preserved in a dessicator.

6. Adsorption Experiments at Room Temperature

(1) Preparation of Magnetite

Magnetite powder was synthetically prepared by controlled oxidation\(^{(5)}\) of Fe(OH)\(_2\) using KNO\(_3\) in an inert atmosphere at 95°C. The magnetite obtained was centrifuged, treated with 1 m HNO\(_3\) for 1 h, washed and dried at 85°C.
(2) Adsorption of Mg$^{2+}$ and Co$^{2+}$ Ions over Magnetite

Experiments were carried out to estimate the amount of Mg$^{2+}$ and Co$^{2+}$ ions adsorbed over magnetite powder. One point five litres of 2 ppm Mg$^{2+}$ solution as Mg(OH)$_2$ was prepared and its pH was adjusted to 10 using LiOH. A hundred mg of magnetite powder was added and the solution was kept agitated using a magnetic stirrer. Samples of solution after filtering the magnetite particles were taken periodically and analyzed for Mg$^{2+}$ using AAS at 285.3 nm. The experiment was carried out in Mg$^{2+}$ containing solution at different pH values in the range 5 to 10. Similar procedure was adopted for the estimation of cobalt adsorbed over magnetite. Cobalt was estimated using AAS at 240.7 nm.

(3) Adsorption Experiments using $^{60}$Co Tracer

Autoclaved carbon steel and Monel-400 coupons were immersed in a pH 10 solution containing $^{60}$Co tracer. The above solution after adjusting the pH to 10 by LiOH was kept overnight and filtered to remove any precipitate.

Two sets of experiments were carried out, one with the coupons prepared in the presence of Mg$^{2+}$ ion and the other with the coupons prepared in the absence of Mg$^{2+}$. Coupons were withdrawn periodically and gamma counting of the coupon was carried out using a single channel analyzer to estimate the $^{60}$Co pick-up.

(4) Zeta Potential Measurements

Zeta potential of magnetite and magnesium adsorbed magnetite was measured using Malvern Zetasizer III equipment. The measurements were made at pH 10.

### III. Results

1. Corrosion Experiment Results

   (1) Carbon Steel

   The observed thicknesses of the oxide, iron release rates and the corrosion rates of carbon steel exposed for a period of 7 days to water containing LiOH (pH 10) at 25°C with and without Mg$^{2+}$ are given in Table 2. A set of five repeat measurements were made under identical conditions and the average values are given in Table 2. The thickness of oxide film was found to be 0.6 μm as compared to more than 1 μm observed in the absence of Mg$^{2+}$. Coupons were withdrawn periodically and gamma counting of the coupon was carried out using a single channel analyzer to estimate the thickness of oxide, estimation of relative thicknesses of oxide layers formed over Incoloy-800 were made as shown in Fig. 3. It was found that the thickness of the oxide as measured by ESCA was lesser in the coupon exposed to solution containing magnesium. Thus, it is evident that magnesium affects the corrosion of Incoloy-800.

   (2) Incoloy-800

   In PHWRs, the main source of cobalt is nickel bearing alloys which contain cobalt as impurity. Monel-400 and Incoloy-800 are used as steam generator tube materials. Control of corrosion and release of corrosion products from these materials will definitely have an impact on the radiation field build-up in the coolant system. Attempts to measure the oxide thickness and other corrosion parameters by the weight loss method was not successful as the amount of oxide formed over this material in the short duration of 7 days was very small and the weight changes were below the detection limit of the weight loss method.

   ESCA results of the oxide layer formed over Incoloy-800 specimen exposed to magnesium containing solution showed that magnesium gets incorporated into the oxide layers as shown in Fig. 1. Presence of magnesium was indicated by the Mg 1s, peak at 1,305 eV and was confirmed by the Mg KLL Auger peak at 305 eV. Depth profile of magnesium in Incoloy-800 showed that it was present in the inner layers of the oxide too, but its concentration was highest in the top layer and exhibited a decreasing trend while going from top to the bottom layer and approached zero as the base metal is approached as shown in Fig. 2. From the oxygen profile of the oxide, estimation of relative thicknesses of oxide layers formed over Incoloy-800 were made as shown in Fig. 3. It was found that the thickness of the oxide as measured by ESCA was lesser in the coupon exposed to solution containing magnesium. Thus, it is evident that magnesium affects the corrosion of Incoloy-800. The elemental depth profile of the oxide layer formed over Incoloy-800 is given in Fig. 4.

   (3) Monel-400

   Monel-400 coupons were also analyzed by ESCA after they were autoclaved. They were found to have a very thin layer of oxide. Coupons exposed to solution containing Mg$^{2+}$ were found to have thinner layer of oxide. Peaks corresponding to Ni 2p$^3/2$ and Cu 2p$^3/2$ contained significant proportion of metal in its zero oxidation state indicating that most of the surface remains unoxidised even in the top layer of the metal. However, presence of magnesium could not be clearly established by ESCA in the oxide layer of this material. As observed in Incoloy-800, weight loss measurements were not of use.
because the oxide formed and corrosion rates were extremely small to measure with confidence.

(4) SUS-304

Besides Incoloy-800 and Monel-400, stainless steels of 300 and 400 series are used in other components of PHWR primary heat transport system circuits but their surface areas are relatively small. SUS-304 coupons exposed to magnesium containing solution in the autoclave showed the presence of magnesium in the oxide layer. Figure 5 shows the peak corresponding to Mg 1s₁/₂.
Analysis of the XPS spectra of elements constituting the SUS-304 were also made and the peak positions for the various elements in the oxide layer are given in Table 3. Cr 2P3/2 peak is expected at 574.4 eV if chromium is in Cr state and at 577 eV if it is in Cr3+ state(s). Peak position of 577.3 eV observed for chromium (Cr 2P3/2) in this material is an indication that chromium exists as Cr3+ in the oxide layer. The peak corresponding to iron was broad and was found to be composed of two peaks. Fe 2P3/2 peak is expected at 709 and 711.4 eV for Fe2+ and Fe3+, respectively. Observation of these two peaks indicated that iron ions in different oxidation states (Fe2+, Fe3+) exist in the oxide layer. The ratio of peak area of Fe2+ to that of Fe3+ was found to be 0.43 in the oxide formed in the absence of magnesium where as the value was 0.37 in the oxide formed in the presence of magnesium. Peak area estimation of the nickel peak revealed that top layers of oxide formed in the presence of magnesium contained lower amount of Ni2+ (0.1%) than that formed in the absence of magnesium (1.5%). This indicates that Mg2+ occupies the divalent metal ion positions which otherwise would have been occupied by Ni2+ and Fe2+.

SEM photographs of some of the coupons of the above mentioned materials autoclaved in the presence of 100 ppb magnesium are given in Photo. 1. Crystalline oxides were found to be formed under this condition on carbon steel and Incoloy-800. Crystallites on Monel-400 could not be seen under the magnification used. No adverse localised effects such as pitting type of attack were observed on any of these materials.

Table 3  Peak position of iron, chromium and nickel observed in autoclaved SUS-304 (Binding energy in eV)

<table>
<thead>
<tr>
<th></th>
<th>Fe 2P3/2</th>
<th>Cr 2P3/2</th>
<th>Ni 2P3/2</th>
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<tbody>
<tr>
<td>2P3/2</td>
<td>710.4</td>
<td>574.4</td>
<td>758.6</td>
</tr>
<tr>
<td>2P3/2</td>
<td>723.7</td>
<td>577.3</td>
<td>855.4</td>
</tr>
</tbody>
</table>

Fig. 3 Variation in oxygen atomic conc.(%) in Incoloy-800 autoclaved in the absence (a) and presence of 100 ppb Mg2+ (b) as a function of depth

Fig. 4  Elemental depth profile in the oxide layer of Incoloy-800 autoclaved in the presence of Mg2+.
Fig. 5 Mg 1s\(\frac{1}{2}\) peak in SUS-304 autoclaved in the presence of Mg\(^{2+}\)

Photo. 1 SEM photographs of PHWR PHT system structural materials exposed to Mg\(^{2+}\) at 265 °C
(a) CS (×1,600), (b) Monel-400 (×6,400), (c) SUS-304 (×8,000), (d) Incoloy-800 (×9,600)
2. Room Temperature Adsorption Studies

The results from the room temperature experiments showed that the rate of magnesium ion adsorption on magnetite was rather fast. It reached a saturation value within 30 min. The amount of magnesium adsorbed per gram of magnetite increased with increase in pH of the medium as shown in Fig. 6. Cobalt adsorption on magnetite also showed a similar trend. However, the amount of adsorption in mol/g was found to be lower than that of magnesium. A good indicator of surface adsorption is the alteration of surface charge subsequent to ion adsorption. Zeta potential measurements carried out at ambient temperature and at pH 10 gave values of $-25 \text{ mV}$ and $-14.9 \text{ mV}$ for magnetite and magnesium adsorbed magnetite, respectively, indicating that the adsorbed magnesium ion shifts the potential towards more positive values.

Room temperature cobalt ion adsorption studies, carried out on the autoclaved carbon steel and Monel-400 coupons, showed that there was not much difference in the amount of cobalt picked-up on coupons of same material autoclaved in the presence and absence of magnesium as shown in Fig. 7. The amount of cobalt adsorbed on Monel-400 was found to be much lower than that on carbon steel surface.

IV. DISCUSSION

1. Corrosion Experiment

Spinels can be represented by the general formula $AB_2O_4$ where 'A' is the divalent metal ion and 'B' is the trivalent ion. Among the transition metals of importance in the context of water cooled nuclear reactor structural materials, chromites and ferrites are usually encountered. They assume normal, inverse and random spinel structures as shown below:

Normal: \[ [A]_{T} [B_2]_{o} O_4 \quad \tau = 0 \]
Inverse: \[ [B]_{T} [A]_{o} O_4 \quad \tau = 1 \]
Random: \[ [A_{(1-\tau)}B_T]_{T} [A_{\tau}B_{(2-\tau)}]_{o} O_4 \quad 0 < \tau < 1, \]

where 't' and 'o' refer to tetrahedral and octahedral holes in which the cations position themselves and 'r' is known as the inversion parameter. The value of 'r' is decided by the nature of $A^{2+}$ and $B^{3+}$ ions. Chromites having normal spinel structures are formed in the inner oxide layers of chromium containing alloys such as stainless steels and in BWRs, it is this layer which picks-up most of the $^{60}Co$. Addition of zinc to the coolant enables the formation of zinc chromite in that layer. Using the site preference energies of transition metal ions in spinel lattices, Lister has computed net relative lattice site energies and has shown that formation of zinc chromite, which is a
normal spinel, is favoured thereby enabling rejection of cobalt and other metal ions from getting incorporated in the inner layer of the oxide. In addition, zinc modifies the oxide layer in such a way that the corrosion and release rates of structural materials are reduced significantly. The combined effect of all the factors leads to radiation field reduction in BWRs. The impact of zinc on the outer oxide layer is not significant. The outer layer consists mostly oxides of iron such as hematite, magnetite and nickel ferrites. The magnetite and nickel ferrite have inverse spinel structure. Zinc ion is destabilised in the octahedral hole of the inverse spinel structure.

Primary heat transport systems of PHWRs contain large surfaces which does not have chromium where the dominant oxide both in inner and outer layers are bound to be ferrites such as magnetite and nickel ferrite. Cobalt ion forms cobalt ferrite which is again an inverse spinel. It is desirable that the ion added to inhibit the cobalt pick-up on these surfaces should form an oxide with inverse spinel structure so that formation of cobalt ferrite is hindered. Based on these considerations magnesium ion was chosen as an alternative to zinc ion to passivate these surfaces.

Magnesium forms MgFe$_2$O$_4$ with inverse spinel structure indicating that magnesium ion is stabilized in the octahedral holes of the oxide lattices of ferrites. Also, from the lattice energy considerations, the order of preference of formation decreases as

$$\text{MgFe}_2\text{O}_4 > \text{Fe}_3\text{O}_4 > \text{CoFe}_2\text{O}_4.$$  

Thus, magnesium increases the stability of the oxide in relation to Fe$_3$O$_4$ which in turn would help to further decrease the tendency to pick-up cobalt. In addition, just as zinc, iron, cobalt and nickel form chromites with normal spinel structures, magnesium also forms magnesium chromite (MgCr$_2$O$_4$) with normal spinel structure. Here again, the structural considerations indicate that magnesium ions would be stabilised in the tetrahedral sites of the normal spinel structure of chromites.

In the present work incorporation of magnesium in the oxide layers formed over the PHT system structural materials has been established. Observation of magnesium in the inner layers of the oxide formed over Incoloy-800 indicates that the magnesium is not simply adsorbed on the surface of oxide, it has been incorporated into the lattices of the oxide. It has also been observed that the presence of magnesium ion in the solution helps to form a thinner oxide layer over carbon steel and Incoloy-800 surfaces. The iron release rates and the corrosion rates of carbon steel were also lower in the presence of magnesium ion. These results are comparable to those observed in carbon steel in the presence of zinc under PHWR PHT system conditions. Also, compatibility studies carried out by other workers have shown that magnesium at ppb levels does not cause stress corrosion cracking on Incoloy-800.

Under alkaline conditions, magnesium ion can exists as Mg(OH)$^+$ or as a mixture of Mg$^{2+}$ and Mg(OH)$^+$. It is expected that the presence of free Mg$^{2+}$ species in solution would favour its incorporation in the oxide surfaces. Species distribution arrived at by calculation from the magnesium ion hydrolysis data at 250°C showed that Mg$^{2+}$ exist in significant proportions and its concentration varies with pH as shown in Fig. 8. Solubility of magnesium hydroxide decreases with increase in temperature (negative temperature co-efficient of solubility) and with increase in hydroxide concentration. The pK of solubility equilibrium (solubility product) of Mg(OH)$_2$ (arrived at by extrapolation of values at 25°C) for 250 and 300°C are 13.5 and 14.5, respectively. The solubility values arrived at from these pK values are 15 and 91 ppb for 290°C, the PHWR core outlet temperature, and 265°C respectively. It is yet to be proved whether magnesium ion at 15 ppb concentration can have the same significant effect that was observed at 100 ppb. Also, the ability of magnesium ion in inhibiting the adsorption of $^{60}$Co on the structural materials at high temperature conditions is yet to be experimentally proved.

2. Low Temperature Adsorption Studies

Low temperature adsorption of magnesium and cobalt ions over magnetite surface is believed to take place through a different mechanism. Metal ions on the
surfaces of the oxides are hydrolysed and the hydrolysed surface metal ions can exchange the H⁺ ion for a metal ion

\[
\text{Fe}^{\delta+} \leftrightarrow \text{O} \rightarrow \text{O}^{\delta-} \rightarrow \text{Fe} \leftarrow \text{O} \leftarrow \text{Mg}
\]

The reaction is limited by the surface area of the oxide. Increase in adsorption of Co²⁺ and Mg²⁺ with increase in pH is attributed to the removal of H⁺ by the neutralization reaction with OH⁻ in the first step of the above reaction sequence. Preferential adsorption of ions over the oxide surface can alter the surface charge of magnetite. Hence, there is a measurable change in the zeta potential.

The relatively lesser amount of either Mg²⁺ or Co²⁺ pick-up on the autoclaved Monel-400 in comparison to carbon steel was attributable to the lower surface area of the oxide in Monel-400 which has very thin oxide and the oxide coverage is not complete as evident from the observation of peaks corresponding to metallic constituents. No difference in the activity pick-up was observed on the carbon steel and Monel-400 coupons autoclaved with and without magnesium. This indicated that mere presence of magnesium on the oxide lattice did not result in decreased pick-up of cobalt.

Difference in the adsorption of cobalt ion and magnesium ions on magnetite surface essentially stems from the availability of suitable ionic species in solution which may be less in the case of cobalt.

**V. CONCLUSIONS**

1. Thickness of magnetite layer formed on carbon steel surface in the presence of 100 ppb magnesium ion at 265°C was lower by a factor of 2 than that of magnetite formed in the absence of magnesium.
2. Corrosion and corrosion product release rates of carbon steel were also found to be low when it was exposed to magnesium containing solution.
3. ESCA of the Incoloy-800 and SUS-304 coupons, exposed in the autoclave to magnesium containing solution at pH₂₅°C 10 and at 265°C showed the presence of magnesium in percentage levels.
4. The depth profile of magnesium in the oxide film on Incoloy-800 showed that its concentration was the highest in the top layers and decreased with depth tending to zero as the base metal was approached.
5. Oxide thickness measurements on carbon steel and Incoloy-800 indicated the possible passivation behaviour of magnesium ion on these surfaces.

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