B. 6 “SCC of Alloys 600, 690, 182, 82, 152 and 52 in PWR Primary Water,”
by Peter M. Scott

Introduction

Nickel base alloys are attractive for PWR primary circuit components because of the close similarity of their coefficients of thermal expansion to that of the low alloy steels used to fabricate the reactor pressure vessel, pressurizer and steam generator shells, as well as their low general corrosion and corrosion product release rates in PWR primary and secondary water. A list of PWR components where Alloys 600 and 690 and their compatible weld metals are used in PWRs is given in Table B.6.1. Typical compositions are shown in Table B.6.2.

Table B.6.1 PWR Components Fabricated from Nickel Base Alloys

<table>
<thead>
<tr>
<th>PWR Components</th>
<th>Nickel Base Alloy Grades Used</th>
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</thead>
<tbody>
<tr>
<td>Steam generator tubes</td>
<td>Alloys 600 MA &amp; TT, 690TT (&amp; 800)</td>
</tr>
<tr>
<td>Steam generator divider plates</td>
<td>Alloys 600 &amp; 690</td>
</tr>
<tr>
<td>Upper head penetrations</td>
<td>Alloys 600 &amp; 690</td>
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<tr>
<td>Lower head penetrations</td>
<td>Alloy 600</td>
</tr>
<tr>
<td>Core supports</td>
<td>Alloy 600</td>
</tr>
<tr>
<td>Pressurizer nozzles</td>
<td>Alloys 600 &amp; 690</td>
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<tr>
<td>Safe ends</td>
<td>Alloy 600</td>
</tr>
<tr>
<td>Weld metal deposits</td>
<td>Alloys 82, 182, 52 &amp; 152</td>
</tr>
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</table>

The susceptibility of Alloy 600 to Intergranular Stress Corrosion Cracking (IGSCC) in high temperature water was first revealed in laboratory testing in 1957 and then in operational service in PWR primary water from the early 1970s. IGSCC following exposure to the primary side environment is today commonly referred to in the industry as Primary Water Stress Corrosion Cracking (PWSCC).\[1,2] Initially, highly cold worked components were affected such as tight U-bends in steam generator tubes and rolled or explosively expanded, cold-worked transitions in diameter of the tubes within the tube sheet[3]. This then became a major cause of steam generator tube cracking in the 1980s, and later, premature steam generator retirement and replacement. PWSCC of pressurizer nozzles and control rod drive mechanism (CRDM) nozzles in the upper heads of PWR reactor pressure vessels followed in the late 1980s and has continued for over a decade [4,5]. CRDM nozzle cracking appeared first in French PWRs in 1991 but was not widely observed elsewhere until the last five years or so.

Apparently interdendritic, but in fact intergranular, stress corrosion cracking (along dendrite “packet” boundaries) of the weld metals Alloys 182 and 82, the former having a composition similar to Alloy 600 (Table B.6.2), has also been observed in recent years in major primary circuit welds of several plants, often after very long periods in service ranging between 17 and 27 years [4,5].

A more detailed description of PWSCC observed in each type of nickel alloy PWR component and the phenomenology of PWSCC in various nickel base alloys is summarized below. A brief description of the methodologies developed to predict and mitigate cracking until, as is often the case, replacement becomes unavoidable, is also
given. When Alloy 600 components are replaced, it is usually by Alloy 690 and its compatible weld metals, Alloys 152 and 52, which have so far proved resistant to PWSCC both in laboratory tests and, to date, after up to 16 years in service. Alloy 800 steam generator tubes have also proved resistant to PWSCC without any known cracking in primary water service.

Table B.6.2 Some Composition Specifications for Nickel Base Alloys Used in PWRs

<table>
<thead>
<tr>
<th></th>
<th>Alloy 600</th>
<th>Alloy 182</th>
<th>Alloy 82</th>
<th>Alloy 690</th>
<th>Alloy 152</th>
<th>Alloy 52</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>&gt;72.0</td>
<td>Bal.</td>
<td>Bal.</td>
<td>&gt;58.0</td>
<td>Bal.</td>
<td>Bal.</td>
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<tr>
<td>Chromium</td>
<td>14-17</td>
<td>13-17</td>
<td>18-22</td>
<td>28-31</td>
<td>28-31.5</td>
<td>28-31.5</td>
</tr>
<tr>
<td>Iron</td>
<td>6-10</td>
<td>≤10.0</td>
<td>≤3.00</td>
<td>7-11</td>
<td>8-12</td>
<td>8-12</td>
</tr>
<tr>
<td>Titanium</td>
<td>≤1.0</td>
<td>≤0.75</td>
<td>≤0.50</td>
<td>≤1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>≤1.10</td>
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<tr>
<td>Niobium plus</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.2-2.2</td>
<td>≤0.10</td>
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<tr>
<td>Tantalum</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molybdenum</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>≤0.50</td>
<td>≤0.05</td>
</tr>
<tr>
<td>Carbon</td>
<td>≤0.05</td>
<td>≤0.10</td>
<td>≤0.10</td>
<td>≤0.04</td>
<td>≤0.045</td>
<td>≤0.040</td>
</tr>
<tr>
<td>Manganese</td>
<td>≤1.0</td>
<td>5.0-9.5</td>
<td>2.5-3.5</td>
<td>≤0.50</td>
<td>≤5.0</td>
<td>≤1.0</td>
</tr>
<tr>
<td>Sulfur</td>
<td>≤0.015</td>
<td>≤0.015</td>
<td>≤0.015</td>
<td>≤0.015</td>
<td>≤0.008</td>
<td>≤0.008</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>≤0.030</td>
<td>≤0.030</td>
<td></td>
<td>≤0.020</td>
<td>≤0.020</td>
<td></td>
</tr>
<tr>
<td>Silicon</td>
<td>≤0.5</td>
<td>≤1.0</td>
<td>≤0.50</td>
<td>≤0.50</td>
<td>≤0.65</td>
<td>≤0.50</td>
</tr>
<tr>
<td>Copper</td>
<td>≤0.5</td>
<td>≤0.50</td>
<td>≤0.50</td>
<td>≤0.5</td>
<td>≤0.50</td>
<td>≤0.30</td>
</tr>
<tr>
<td>Cobalt</td>
<td>≤0.10</td>
<td>≤0.12</td>
<td>≤0.10</td>
<td>≤0.10</td>
<td>≤0.020</td>
<td>≤0.020</td>
</tr>
</tbody>
</table>

Alloy 600 steam generator tubes

Most PWR steam generators are of the ‘recirculating’ type although some are ‘once-through’ where all the secondary water entering the steam generator is transformed into steam. Most in-service PWSCC has occurred in recirculating steam generators. An important difference between the two from the point of view of PWSCC is that the once-through steam generators were subjected to a pre-service stress relief of the whole steam generator at a temperature of about 610 °C (1130 °F). In addition to provoking grain boundary carbide precipitation in Alloy 600, some grain boundary chromium depletion (sensitization) also occurred. The lower strength and grain boundary carbide
precipitation in once-through steam generators tubes has proved to be advantageous for resistance to PWSCC on the primary side, despite the sensitization, although even these steam generators are now being steadily replaced after typically 20 to 25 years service [6]. In one case, however, an accidental ingress of thiosulfate into the once-through steam generators led (predictably) to extensive intergranular attack (IGA) of the sensitized tubes.

PWSCC of Alloy 600 steam generator tubing in the mill annealed (MA) condition became a major degradation mechanism from the 1970s onwards for recirculating steam generators [7]. In 1971, the first confirmed primary side cracking of mill annealed Alloy 600 tubes of recirculating steam generators occurred when leakage at U-bends was experienced in the Obrigheim steam generators after only 2 years of operation [2]. Cracking occurred both in the tight U-bends, mainly on the inner two rows at the apex and at the tangent points as well as in the tube sheet at the transition expansion or roll expansion regions of the tubes. The latter has been responsible for premature steam generator replacement at a number of plants.

The first roll transitions experiencing PWSCC were located on the hot leg side where the temperature is typically around 320 °C (610 °F) and is 30 to 40 °C (55 to 70 °F) hotter than the cold leg inlet at 280 °C (535 °F). Thus, it was clear that temperature had a significant influence on PWSCC, indicating a strongly thermally activated process. The apparent activation energy from fitting the temperature dependence to the Arrhenius equation is rather high (~ 180 kJ/mole) so that a typical temperature difference of 30 °C (55 °F) between hot and cold legs could easily account for a factor of four to five increase in the time to the onset of detectable cracking. Thus, reduction of hot leg temperature has been one possible mitigating action that has been used. Hot leg temperature reductions from 4 to even 10 °C have been applied.

The magnitude of the tensile stresses, particularly residual stress from fabrication, has also had a major impact on the time for detectable PWSCC to develop; only the most highly strained regions of steam generator tubing (that is, row-one and two U-bends, initially, and subsequently larger radius tubes, roll transition regions, expanded regions, and dented areas) have exhibited PWSCC. Consequently, several stress mitigation techniques have been evolved such as local stress relief of first and second row U-bends by resistance or induction heating, and shot peening or rotopeening to induce compressive stresses on the internal surface of roll transitions [8,9]. While peening helps to limit initiation of new cracks, it cannot prevent the growth of existing cracks whose depth is greater than that of the induced compressive layer, typically 100 to 200 μm. Thus, peening has been most effective when most tubes have either no cracks or only very small ones, i.e. when practiced before service or very early in life [9,10].

Material susceptibility, in combination with the factors mentioned above, is also a major factor affecting the occurrence of PWSCC in service. Most PWSCC has occurred in mill annealed tubing. However, it is important to emphasize that there is not a single product called "mill-annealed" Alloy 600 tubing since each tubing manufacturer has employed different production processes. Whereas some mill-annealed tubing has not experienced any PWSCC over extended periods of operation, in other cases it has occurred after only 1 to 2 years of service, particularly at roll transitions. This variability of PWSCC susceptibility is even seen between heats from the same manufacturer in the same steam generator [11]. The variation in susceptibility to PWSCC of the heats of Alloy 600 typically fits approximately a lognormal distribution so that a rather small fraction of Alloy
600 heats may be responsible for a disproportionately high number of tubes affected by primary side PWSCC. The reasons for such variability are only partly understood.

This microstructural aspect of susceptibility to PWSCC has been observed to be strongly affected by the final mill-annealing temperature, which determines whether carbide precipitation occurs predominantly on grain boundaries or intragranularly. The most susceptible microstructures are those produced by low mill-annealing temperatures, typically around 980 °C (1800 °F) that develop fine grain sizes (ASTM 9 to 11), copious quantities of intragranular carbides, and, usually, few if any intergranular carbides [12,13]. Higher mill annealing temperatures in the range of 1040 to 1070 °C (1900 to 1960 °F) avoid undue grain growth and leave enough dissolved carbon so that intergranular carbide precipitation occurs more readily during cooling.

A further development to exploit the apparent advantages of grain boundary carbides for PWSCC resistance was to thermally treat the tubing for ~15 h at 705 °C (1300 °F) after mill annealing. This both increases the density of intergranular carbides in the grain boundary and provides enough time so that most of the carbon in solution is consumed, and the chromium can diffuse to eliminate its depletion profile and thus avoid sensitization [13]. The beneficial influence of grain boundary chromium carbides on primary side PWSCC resistance has been extensively evaluated in laboratory studies and suggests an improvement in life of thermally treated tubing of between 2 and 5 times relative to the mill annealed condition. In fact, primary side PWSCC resistance is improved with or without grain boundary chromium depletion, as also deduced from the generally much better operating experience of Alloy 600 tubing of once-through steam generators [6,12,13]. However, even thermally treated Alloy 600 tubing has cracked in service, although much less frequently than mill annealed Alloy 600. This has usually been attributed to a failure of the thermal treatment to produce the desired intergranular carbide microstructure either due to insufficient carbon or factors such as tube straightening prior to thermal treatment, which has favored carbide precipitation on dislocations instead of grain boundaries.

Steam generator tubes with PWSCC detectable by non-destructive testing have usually been preventively plugged either to avoid leakage or before the crack length reaches some pre-defined conservative fraction of the critical size for ductile rupture. Where depth-based repair criteria are followed, tubes may also have been preventatively plugged since cracks could not be reliably depth sized. Sleeving has sometimes been deployed as a repair method in operating PWRs to avoid plugging and maintain the affected tubes in service. The sleeves bridge the damaged area and are attached to sound material beyond the damage. The ends of the sleeves may be expanded hydraulically or explosively and are in most cases sealed by rolling, welding, or brazing [3].

Modern (usually replacement) steam generators have been fabricated using Alloy 690 tubes thermally treated for 5 hours at 715 °C. As well as being highly resistant in severe laboratory tests to PWSCC in PWR primary water compared to either mill annealed or thermally treated Alloy 600, the lead steam generators with thermally treated Alloy 690 tube bundles have, to date, about 16 years of service with no known tube cracking.
Thick section Alloy 600 components

Thick section, forged, Alloy 600 components started to crack in the mid 1980’s starting with the hottest components, pressurizer nozzles [11,14]. In France, for example, all pressurizer nozzles were replaced with stainless steel. In 1991, the first cracking of Alloy 600 upper head Control Rod Drive Mechanism (CRDM) nozzles occurred at the Bugey 3 plant in France. At first, it was thought that this could be a special case because of the combination of a stress concentration due to a counter bore in the nozzles just below the level of the J-groove seal weld with the upper head, as well as a relatively high operating temperature that was believed to be closer to that of the hot leg in this first generation French plant. However, the problem spread during the 1990s to CRDM nozzles in other plants with no counter bore, nor with a tapered lower section to the CRDM nozzle, and in upper heads where the temperature was the same as the inlet cold leg temperature [15,16].

Three common features of the cracking of upper head CRDM nozzles were the presence of a significant cold worked layer due to machining or grinding on the internal bore, some distortion or ovalization induced by the fabrication of the J-groove seal welds, and a tendency to occur much more frequently in the outer set-up circles where the angles between the vertical CRDM nozzle and the domed upper head were greatest. The combination of these three features plus the fact that the upper head is stress relieved before the CRDM nozzles are welded in place pointed to high residual stresses being responsible for these premature cracking occurrences.

Although the generic problem of Alloy 600 CRDM nozzle cracking first appeared in France, only sporadic instances of similar cracking were observed in other countries until the beginning of the 21st century, since when numerous other incidents have been reported. In some cases, where cracking was allowed to develop to the point of leaking primary water into the crevice between the CRDM nozzle and the upper head, circumferential cracks initiated on the outer surface of the CRDM nozzle at the root of the J-groove seal weld [17]. This latter observation had also been made in 1991 at Bugey 3 but only to a minor extent. No further leaks of primary water due to CRDM nozzle cracking have occurred in France because of an inspection regime adopted to avoid them and a decision taken to replace all upper heads using thermally treated Alloy 690 CRDM nozzles [15,16]. The same strategy has often been adopted elsewhere as more economic than the cost of repairs and repeat inspections. The dangers of allowing primary water leaks to continue over several years so that extensive boric acid deposits accumulated was amply demonstrated by the discovery of very severe corrosion (wastage) of the low alloy steel of the upper head at the Davis Besse plant in 2002 [5,17].

Nickel base weld metals

The history of PWSCC in Alloy 600 and similar nickel base alloys has continued in recent years with the discovery of cracked Alloy 182 welds in several PWRs around the world [17,18]. This has occurred on the primary water side of the J-groove welds that seal the CRDM nozzles in the upper head and also in a few cases in the safe end welds of the reactor pressure vessel or pressurizer. One case has also occurred in the J-weld of a lower head instrumentation penetration [19]. Cracking seems to be significantly exacerbated by the presence of weld defects and of weld repairs made during fabrication, usually to eliminate indications due to hot cracking, or slag inclusions, thus
again implicating high residual stress in the cracking observed to date. The cracking has often been described as interdendritic but recent work shows that it is in fact intergranular [20]. Incubation periods before detectable cracking seem to be very long, up to twenty years.

It should be noted that all the nickel base weld metal cracking observed to date has concerned welds that have not experienced the stress relief given to adjacent low alloy steel pressure vessel components [18]. Although the stress relief temperature is clearly not optimized for nickel base alloys (or stainless steels), it has been shown on mockups that the surface residual stress of the welds is very significantly reduced and doubtless imparts greater resistance to PWSCC in PWR primary water.

**Life prediction**

In spite of the improvements available for new plants or for replacement components equipped with Alloy 690 and welded with Alloys 52 or 152, many Alloy 600 components, either mill annealed, thermally treated or forged remain in service. While most show no sign of cracking in service, it is important to assess component life and endeavor to predict when replacement may become necessary. Prediction methodologies were first developed for steam generator tubes and later extended to pressurizers and upper head CRDM penetrations. Both deterministic and probabilistic methods have been developed [21,22].

Modeling of Alloy 600 component life is often based on the assumption that the time to detectable cracking varies as the inverse fourth power of the stress (including residual stress) above a threshold stress of ~250 MPa with a temperature dependency approximated by the Arrhenius equation. Despite the scatter observed in determinations of apparent activation energy, there is a reasonable consensus that a value of 180 kJ/mole (44 kcal/mole) is adequate for component life estimations. Some approaches to modeling also attempt to include material variability in susceptibility to PWSCC [22,23,24,25]. However, in the case of classification of the susceptibility of CRDM nozzle cracking in US PWRs this aspect has not been taken into account [17]. Nevertheless, as can be seen in Figure B.6.1, the plants most at risk from PWSCC of Alloy 600 CRDM nozzles have been correctly identified.
Application of the Weibull distribution to quantify the dispersion in stress corrosion data is well established and has generally been successfully applied to PWSCC in Alloy 600 steam generator tubes and upper head penetrations [21,22]. The dispersion in times to observe detectable cracks arises from the inherent variability in susceptibility of materials to stress corrosion cracking and, in the case of plant components, to uncertainty in the stress and temperature. The Weibull distribution can be fitted to the early observations of PWSCC as a function of operating time and provides an effective tool for predicting the future development of cracking so that informed inspection and repair plans can be formulated [21]. An alternative Monte Carlo simulation approach to improving the stochastic prediction of PWSCC has also been developed in the context of upper head penetration cracking taking into account the inherent dispersion in the input parameters of stress, temperature, activation energy and material susceptibility [22,23,24,25].

Another parameter that can have a dramatic influence on component susceptibility to cracking in service is the quality of the surface finish due to machining, grinding etc. Based on careful characterizations of the thicknesses of cold worked layers and residual stresses left by different machining techniques, a quantitative framework for assessing their impact on component resistance to PWSCC has been developed [14,23,24,25].

Once a stress corrosion crack has been detected by non-destructive examination in a PWR primary circuit component, an essential step in the justification of structural integrity and further operation without repair or replacement of the affected component is an assessment of crack growth during the next few operating cycles. Practical approaches to assessing crack growth by PWSCC in Alloy 600 components have relied on empirical measurements of crack growth rates as a function of crack tip stress intensity, $K_I$, as follows [26,27]:

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**Figure B.6.1** Equivalent damage years for the upper head CRDM nozzles of US PWRs in September 2002 [17]

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The values of the coefficients C and n vary for given practical circumstances, but there is a reasonable consensus that the apparent activation energy to be used for adjusting the coefficient C for temperature is \( \sim 130 \text{ kJ/mole} \), which is somewhat lower than the value quoted above for overall life prediction, where time to crack initiation usually dominates.

Other variables that are known to influence the rate of crack growth in Alloy 600 are cold work, hydrogen overpressure and possibly pH or lithium hydroxide concentration. Cold work can easily affect the value of the coefficient C by as much as an order of magnitude. Hydrogen overpressure effects are also potentially significant [28]. However, the effect has not been explicitly included in crack growth assessment equations to date, probably because the hydrogen concentration in PWR primary water is controlled within a relatively narrow range. Concerning the possible influence of pH or lithium concentration in PWR primary water on crack growth kinetics, the effect is, at most, small within the range of pH or lithium concentrations permitted by the PWR primary water specification [11,22]. More recent work suggests that the effect of lithium within this range is virtually non-existent [29].

**Summary of laboratory investigations**

As early as 1957, laboratory studies of cracking of high-nickel alloys in high-purity water at 350 °C (660 °F) were reported [1,5] although at that time the importance of the corrosion potential as fixed by the hydrogen partial pressure was not understood. During the following years, numerous laboratory tests were performed in different environments to duplicate and explain these observations. Nevertheless, despite considerable experimental efforts, no consensus exists as to the nature of the cracking mechanism [29] and, as noted above, both remedial measures and life modeling have relied on empirical, phenomenological correlations. The essential phenomenological features of primary water PWSCC of Alloy 600 have, nevertheless, been very well characterized, as follows:

- a profound influence of hydrogen partial pressure (or corrosion potential) and observation of maximum susceptibility centered on corrosion potentials near the Ni/NiO stability equilibrium;
- an apparently continuous mechanism of cracking between 300°C subcooled water and 400°C superheated steam;
- a high and variable apparent activation energy typically 180 kJ/mole for initiation but with a scatter band of 80 to 220 kJ/mole;
- a strong influence of carbon content and microstructure, particularly a favorable influence of grain boundary carbides and an undesirable effect of cold work;
- a high stress exponent of \( \approx 4 \) for lifetime to cracking occurrence.

It can be noted that despite differing opinions about the mechanism of PWSCC of Alloy 600, most recent models incorporate the idea that solid state grain boundary diffusion is rate controlling [30]. Such models provide physically based support for the empirical value of the activation energy, which is typical of solid-state grain boundary diffusion in nickel. Physical support for the fourth power dependency on applied stress comes
mainly from studies of grain boundary sliding (itself dependent on grain boundary diffusion) observed during primary creep in Alloy 600 at temperatures between 325 and 360°C [23,31]. Grain boundary sliding rates are also observed to depend on grain boundary carbide coverage, greater coverage being associated with slower grain boundary sliding rates and higher resistance to PWSCC. However, although grain boundary carbide morphology is a major reason for heat-to-heat variability in susceptibility to PWSCC of Alloy 600 in PWR primary water, it is clear that other metallurgical parameters, albeit poorly characterized or unidentified, must be involved.

Research into PWSCC, particularly of thick-walled components made of Alloy 600 and its weld metals, is ongoing throughout the world and significant progress, both in practical assessment of service life and mitigation measures, as well as in more fundamental understanding, is anticipated within the next few years.

Alloy 690 has been extensively tested in the laboratory in order to quantify its resistance to PWSCC and to estimate the advantage gained relative to Alloy 600 (32). The improvement factor for thermally treated Alloy 690 relative to mill annealed Alloy 600 has been determined to be greater than 26, and greater than 13 relative to thermally treated Alloy 600. These factors have been judged to be sufficient to conclude that cracking is unlikely in 60+ years. The corresponding weld metals, Alloys 152 and 52, have also been tested although to a lesser extent than the base material but nevertheless appear to have similar resistance to Alloy 690.

Some knowledge gaps have been identified apart from an insufficient data base for Alloy 152 and 52 weld metals mentioned above (32). One important gap concerns possible effects of product form and subtle changes of composition and mechanical processing effects on PWSCC resistance since it has proved possible to produce structures that can crack under extremely severe test conditions. A potential concern for susceptibility of weld heat affected zones has also been identified by analogy with known data for Alloy 600 and this could also be extended to the mixing zones with stainless and low alloy steels in bimetallic welds. Little information is available on corrosion fatigue properties of Alloy 690 although these are expected to be similar to those of Alloy 600. Possible low temperature crack propagation during transient conditions encountered during plant cooldown has also been identified as requiring some study.
References for B. 6


