Article

Analysis of the Technological Evolution of Materials Requirements Included in Reactor Pressure Vessel Manufacturing Codes

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Abstract: The growth of green energy technologies within the frame of the 7th Sustainable Development Goal (SDG) along with the concern about climatic changes make nuclear energy an attractive choice for many countries to ensure energy security and sustainable development as well as actively address environmental issues. Unlike nuclear equipment (immovable goods), which are often well-catalogued and analyzed, the design and manufacturing codes and their standardized materials specifications can be considered movable and intangible goods that have not been thoroughly studied based on a detailed evaluation of the scientific and technical literature on the reactor pressure vessel (RPV) materials behavior. The aim of this work is the analysis of historical advances in materials properties research and associated standardized design codes requirements. The analysis, based on the consolidated U.S. Nuclear Regulatory Commission (NRC) Regulatory Guide (RG) 1.99 Rev.2 model, enables determination of the best materials options, corresponding to some of the most widely used material specifications such as WWER 15Kh2MFAA (used from the 1970s and 1980s; already in operation), ASME SA-533 Grade B Cl.1 (used in pressurized water reactor-PWR 2nd–4th; already in operation), DIN 20MnMoNi55 and DIN 22NiMoCr37 (used in PWR 2nd–4th) as well as ASTM A-336 Grade F22V (current designs). Consequently, in view of the results obtained, it can be concluded that the best options correspond to recently developed or well-established specifications used in the design of pressurized water reactors. These assessments endorse the fact that nuclear technology is continually improving, with safety being its fundamental pillar. In the future, further research related to the technical heritage from the evolution of materials requirements for other clean and sustainable power generation technologies will be performed.

Keywords: technology; technological advancements; technical heritage; materials science; requirement; degradation; irradiation embrittlement; reactor pressure-vessel; manufacturing code

1. Introduction

The 7th Sustainable Development Goal (SDG), as established by the United Nations for 2030, aims to ensure access to a reliable, sustainable, affordable and modern energy. This issue, along with the growing concern about climatic changes, has provided the impetus required for the growth of green energy technologies. In this context, nuclear energy is a meaningful option, as it is a nearly carbon-free source of power, evaluated over its entire lifecycle [1]. Thus, nuclear power is the choice of many countries to ensure energy security and sustainable development as well as actively addressing environmental issues [2]. Our societies face a tremendous and increasing energy need while needing to mitigate global climate change and preserve the environment [3]. The development of nuclear reactors has followed an evolutionary track of both the technical solution and the questions the
technology is trying to address [4]. Even though accidents at nuclear power plants (NPPs) have potentially devastating consequences, they cannot be completely removed from the current energy portfolio because nuclear power has the smallest full-lifecycle carbon footprint among all energy sources and is one of the cheapest available energy sources [5,6].

In summary, nuclear power is a promising solution to meet worldwide increasing demand for energy, to limit the consumption of non-renewable resources for producing energy and to reduce CO₂ emissions. Many key industrial and scientific processes, such as the generation of nuclear energy, are of enormous social benefit as energy demand and consumption grow over time [7]. In addition, nuclear applications of combined cycles have been the subjects of a recent investigation [8], including small modular reactors (SMRs) [9] and high-temperature reactors for combined electricity/hydrogen production [10]. Safety is the most important aspect to consider in the design and construction stages of a nuclear power plant. Although there are many aspects of reactor safety, the safe operation of a nuclear reactor ultimately hinges on the structural integrity of the components [11]. Reactor pressure vessel (RPV) steels play a critical role in the operation safety of any nuclear power plant. Within a nuclear power plant, there are many components made of steel, such as pipes or high-pressure vessels, in areas subjected to radiation [12,13]. Thus, from this perspective, the most important structural component of a nuclear power plant is the RPV, which is constructed primarily from ferritic steels that have to meet specific requirements in terms of impurity contents [14,15]. Structural materials are key to the containment of nuclear fuel and fission products as well as reliable and thermodynamically efficient production of electrical energy from nuclear reactors. High-performance metallic structural materials will be critical for the future success of proposed fusion energy reactors, which will expose the structures to unprecedented fluxes of high-energy neutrons along with intense thermomechanical stresses [16].

Nowadays, regulations on nuclear and radiological safety tend to be homogenized in all countries of the world; however, they do not reach the same legal formulation, since this is the competence of national parliament legislations. This means that at present there are still serious differences in the nuclear regulations of some countries and therefore in the technological requirements for the manufacture of main components, which are the result of the historical vicissitudes experienced since the beginning of the nuclear age [17]. For this reason, to ensure its safety function, the manufacture and in-service inspection of reactor vessels is carried out according to specific codes or standards; among these are the ASME B&PV code (USA), the–AFCEN codes (France), KTA standards (Germany), GOST standards (Russia), and the JSME code (Japan), to ensure suitable quality and safety. There are several design code possibilities in pressure vessel manufacturing, which is important because engineers must assess the standards early in the design process, at which point some key parameters may still be uncertain [18,19]. The success of nuclear energy relies on materials which provide and sustain a host of high-performance properties [20]. RPV steels must satisfy standard materials design criteria based mainly on an adequate resistance to radiation damage and chemical degradation. In addition, nuclear applications must also consider the nuclear physics characteristics of materials. This additional restriction in nuclear materials engineering poses tremendous challenges but also opportunities in material advancements [21]. We distinguish two main types of degradation mechanisms in steel components that operate in a nuclear reactor environment [22]:

- Corrosion of materials and corrosion erosion, stress corrosion and corrosion-fatigue combined processes;
- Embrittlement by irradiation of the steels of the vessel.

The irradiation embrittlement of RPV ferritic steels is the most influential aging mechanism affecting PWR reactor pressure vessels [14,23].

The Spanish National Plan for Industrial Heritage includes the analysis of goods in three categories: immovable, movable and intangible. Nuclear heritage includes the life cycle of nuclear technology, ranging from its intellectual conception, defining the design requirements, to its testing, implementation, operation and decommissioning.
While all nuclear equipment (immovable) is often well-catalogued and analyzed, design and manufacturing codes and their standardized material specifications (movable and intangible) have not been thoroughly studied based on a detailed evaluation of the scientific and technical literature on the behavior of RPV materials. Thus, the aim of this work is the study of the historical advances on materials properties research and their associated standardized design codes requirements, based on a novel methodology of analysis that combines an extensive technological and scientific literature review with the application of a standardized prediction model. Consequently, more than 80 historical research works have been analyzed in this study, reported in more than 20 books related to radiation effects on reactor pressure vessels. They have been reviewed to draw general conclusions on the behavior of the materials most used in the manufacture of RPV and on their technical specifications.

2. Methods

The methodology of the performed analysis is divided into 3 stages (Figure 1).

- Stage 1. Review of the first steps in nuclear technology development and the materials technology evolution: main milestones of the nuclear era (Section 2.1.1) and review of contemporary data and theory regarding RPV steel embrittlement for a suitable materials selection (Section 2.1.2).
- Stage 2. Radiation damage: review of the ASTM Special Publications dedicated to radiation effects on metals.
- Stage 3. Analysis of the evolution of chemical composition restrictions in historical materials used in the RPV manufacturing.
- Stage 4. Application of U.S. NRC R.G. 1.99 to estimate \( \Delta RT_{DBT} \) for the historical and recent materials to analyze the effect of requirements' evolution.

2.1. Stage 1.—Review of the First Steps in Nuclear Technology Development and Materials Technology Evolution

This stage of the methodology provides a review of the main milestones of the civil nuclear era (Section 2.1.1) and a review of the state of the art of the RPVs steel embrittlement for a suitable materials selection (Section 2.1.2).

2.1.1. Main Milestones of the Nuclear Era

In 1938, it was confirmed that the nucleus of an atom could actually be split in two (fission) and the fission of an atom resulted in a release of energy; subsequently, nuclear power generation became feasible. Important milestones in the history of nuclear technology and energy are shown in Table 1.
Table 1. Main milestones of the nuclear technological era [24,25].

| Chronology       | Description                                                                                                                                                                                                                                                                                                                                 | Type   |
|------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------|
| 1939 January     | Otto Hahn and Fritz Strassman report in the journal Naturwissenschaften that they have bombarded and split the uranium atom into two or more lighter elements.                                                                                                                      | •      |
| 1942 December    | The first self-sustaining nuclear chain reaction occurs at the University of Chicago.                                                                                                                                                                                                                                                    | •      |
| 1946 August      | The Atomic Energy Act of 1946 creates the Atomic Energy Commission (AEC) to control nuclear energy development and explore peaceful uses of nuclear energy.                                                                                                                                                                             | ◦      |
| 1951 December    | In Arco, Idaho, Experimental Breeder Reactor I produces electric power, lighting four light bulbs.                                                                                                                                                                                                                                        | •      |
| 1953 March       | Nautilus starts its nuclear power units for the first time.                                                                                                                                                                                                                                                                              | •      |
| 1953 December    | President Eisenhower delivers his “Atoms for Peace” speech before the United Nations.                                                                                                                                                                                                                                                      | ◦      |
| 1954 August      | President Eisenhower signs The Atomic Energy Act of 1954, the first major amendment of the original Act.                                                                                                                                                                                                                                  | ◦      |
| 1955 January     | The AEC announces the Power Demonstration Reactor Program.                                                                                                                                                                                                                                                                               | ◦      |
| 1955 July        | Arco, Idaho, population 1000, becomes the first town powered by a nuclear powerplant.                                                                                                                                                                                                                                                 | • ◦    |
| 1955 August      | Geneva (Switzerland) hosts the first United Nations International Conference on the Peaceful Uses of Atomic Energy.                                                                                                                                                                                                                         | ◦      |
| 1957 July        | The first power from a civilian nuclear unit is generated by the Sodium Reactor Experiment at Santa Susana, California.                                                                                                                                                                                                                   | •      |
| 1957 October     | President Eisenhower delivers his “Atoms for Peace” speech before the United Nations.                                                                                                                                                                                                                                                      | ◦      |
| 1957 December    | The United Nations creates the International Atomic Energy Agency (IAEA) in Vienna, Austria, to promote the peaceful use of nuclear energy.                                                                                                                                                                                                 | ◦      |
| Early 1960s      | Small nuclear power generators are first used in remote areas to power weather stations and to light buoys for sea navigation.                                                                                                                                                                                                             | •      |
| 1961 November    | The U.S. Navy commissions the world’s largest ship, the U.S.S. Enterprise (nuclear-powered aircraft carrier with the ability to operate for up to 740,800 km without refueling).                                                                                                                                                                  | •      |
| 1965 April       | The first nuclear reactor in space (SNAP-10A) is launched by the United States.                                                                                                                                                                                                                                                       | •      |
| 1970 March       | The United States, United Kingdom, Soviet Union and 45 other nations ratify the Treaty for Non-Proliferation of Nuclear Weapons.                                                                                                                                                                                                          | ◦      |
| 1974 October     | The Energy Reorganization Act of 1974 divides AEC functions in two new agencies: Energy Research and Development Administration (ERDA), to carry out research; and Nuclear Regulatory Commission (NRC), to regulate nuclear power.                                                                                                             | ◦      |
| 1977 October     | Department of Energy (DOE) begins operations.                                                                                                                                                                                                                                                                                    | ◦      |
| 1979 March       | The worst accident in U.S. commercial reactor history occurs at the Three Mile Island nuclear power station near Harrisburg, Pennsylvania. The accident was caused by a loss of coolant from the reactor core due to a combination of mechanical malfunction and human error.                                                      | ◦      |
| 1980 March       | DOE initiates the Three Mile Island accident research and development program to develop technology for disassembling and de-fueling the damaged reactor. The program continued for 10 years and made significant advances in developing new nuclear safety technology.                                           | ◦      |
| 1986 April       | Operator error causes two explosions at the Chernobyl No. 4 nuclear powerplant in the former Soviet Union. The reactor has an inadequate containment building, and large amounts of radiation escape. A plant of such design would not be licensed in the United States or Western Europe. | ◦      |
| 1989 April       | The NRC proposes a plan for reactor design certification, early site permits, and combined construction and operating licenses.                                                                                                                                                                                                     | • ◦    |
| 1990 March       | DOE launches a joint initiative to improve operational safety practices at civilian nuclear powerplants in the former Soviet Union.                                                                                                                                               | ◦      |
| 2000 December    | The last of the reactors at the Chernobyl nuclear power plant are shut down.                                                                                                                                                                                                                                                           | ◦      |
| Early 2004       | The first of the late third-generation units was ordered for Finland—a 1600 MWe European PWR (EPR).                                                                                                                                                                                                                                  | •      |
| 2011 March       | Fukushima Daiichi nuclear power plant accident occurs after a severe earthquake off the coast of Japan. This caused the establishment of more stringent safety specifications for reactors around the world.                                                         | ◦      |
| 2020 July        | ITER begins its assembly with the support of 35 countries.                                                                                                                                                                                                                                                                            | •      |

Note about the type of milestone: Technology → •; Regulation and Public dissemination → ◦; Failures, accidents and learned lessons → ◦.

Among the reactors cooled by light water, the most interesting currently are those of the pressurized water type (Pressure Water Reactor, PWR) and those of boiling water type (Boiling Water Reactor, BWR). Henceforth, we will focus on PWR-type reactor vessels, as they are the most widely used technology in reactors currently operating in the global
Materials of RPVs are exposed to neutron radiation generated by nuclear fission reactions and can experience considerable damage even at very low doses of radiation, causing embrittlement and a shift of the $\Delta RT_{DBT}$. Nanoscale microstructures induced by irradiation obstruct the migration of dislocations. This interaction prevents plastic deformation and induces steel embrittlement [28]. Neutron irradiation degrades the mechanical properties of RPV steels and the extent of the degradation is determined by the type and structure of the steel as well as by other factors, such as neutron fluence, irradiation temperature, neutron flux and chemical composition [29].

A comprehensive explanation of radiation damage in solids was first given by Wigner more than a half century ago [30]. In the case of PWR RPVs, damage is produced mostly by fast neutrons ($E \approx 0.1$ to 15 MeV) in the RPV wall at the height of core [31]. On the basis of Seitz’s theory [32,33], collisions occur between neutrons and lattice atoms and between displaced and lattice atoms. If sufficient energy is transmitted during a collision, the impacted atom will be displaced from its site and knocked into an interstitial position. The effect of irradiation on elastic constants was firstly determined by Charlesby, Hancock and Sansom in 1954 [34]. In the same year, Wilson and Berggren [35] irradiated specimens
of ASTM-A212 Gr. B steel at temperatures lower than 50 °C and verified an increase in the $\Delta RT_{DBT}$.

Under typical operating conditions in a nuclear reactor, chemical composition is more influential on the process of neutron irradiation embrittlement than neutron flux [36] and irradiation temperature [37,38]. Mager [38] did not find apparent dependence between the neutron flux value and the embrittlement of the material, for neutron flux rates from $\phi = 2.5 \times 10^{18} \text{n/cm}^2$ to $\phi = 8.8 \times 10^{19} \text{n/cm}^2$. Porter [36] and Kangilaski [37] determined that the irradiation temperature for which the embrittlement of the material is maximum takes place at temperatures below 230 °C. Pachur [39] showed that an irradiation temperature of 150 °C produces the greatest fragility of the material. This is because an increase in the irradiation temperature favors the repair of defects produced by neutron bombardment, through a process of annealing the material [14]. Figure 3 provides these main contributions to material embrittlement, highlighting the role of chemical composition.

![Figure 3. Main contributions that enhance the radiation embrittlement susceptibility of steels.](image)

Main Technological Characteristics Influencing Irradiation Embrittlement Characteristics

These studies on the influence of the chemical composition, neutron flux and irradiation temperature, under operating conditions of nuclear reactors are considered still valid today since they have been confirmed by analyzing the materials from reactors that have been in operation for decades [40–43]. Therefore, nowadays, it is a proven fact that the effect of neutron flux on the brittle–ductile behavior of the material is a complex phenomenon dependent on the composition of the alloy and on temperature [44].

Main Technological Characteristics Influencing Irradiation Embrittlement Characteristics

The weight percentages of copper, phosphorus and nickel are important parameters in RPV steels [45], the first two being the ones that most affect irradiation embrittlement. Copper-rich precipitates, which act as barriers to the dislocation motion on the slip plane, have been recognized as contributing to radiation hardening in irradiated alloys [46]. A model analysis for Cu-rich precipitates and an empirical logarithmic law for relaxation of residual stress demonstrated that an increment of the embrittlement due to Cu-rich precipitates increases with Cu and Ni contents and is proportionate to yield stress change, which is related to irradiation hardening [47]. In 1996, Odette et al. [48] concluded that a Cu wt.% content greater than 0.1 wt.% generates copper-rich precipitates that are responsible for irradiation embrittlement of nuclear primary loop materials. Odette et al. studied the influence of Cu wt.% in twenty-two samples with different concentrations of this element, irradiated with a neutron flux between $\phi = 0.76 \times 10^{16} \text{n/cm}^2$ and $\phi = 7.1 \times 10^{22} \text{n/cm}^2$ (this range includes the neutron flux $\phi = 5 \times 10^{19} \text{n/cm}^2$ used in material monitoring programs according to the KTA 3203 standard), at temperatures between 260 and 315 °C. Odette et al. concluded that for Cu levels below 0.1%, copper-rich precipitates responsible for radiation hardening in materials generating a shift of the ductile-to-brittle transition temperature ($\Delta RT_{DBT}$) are not formed. When the Cu wt.% content is greater than 0.1%, the increase in the $\Delta RT_{DBT}$ due to embrittlement by irradiation is greater the higher the Cu wt.% content, verifying that it shows a linear behavior with the Cu content up to a value between 0.25 and 0.3% [49]. Specifically, it has been proven that, under the operating conditions of nuclear reactors, ultrafine Cu precipitates formed within the materials are responsible for radiation-induced embrittlement [50]. Likewise, in these types of steels with Ni content (MnMoNi steels), the precipitates that are formed have been shown experimentally [51] to not contribute to the over-aging or softening of the material. Ni increases the volume and action of Cu precipitates [49]. Some research works, such as those of Petrequin et al. [52],
Stofanak et al. [53] and Nikolaeva et al. [54], concluded that, for values lower than 1% of Ni, no negative effects are observed on the mechanical properties of materials [14]. In addition, it has been experimentally demonstrated that a P wt.% content greater than 0.02 wt.% negatively affects the mechanical properties of the material because it increases the brittleness of the material at higher temperatures. For similar irradiation conditions (neutron flux interval between $\phi = 1 \times 10^{19}$ n/cm$^2$ and $\phi = 5 \times 10^{20}$ n/cm$^2$, covering the interval according to KTA 3203 [55]) and temperature (340–460 °C), it has been experimentally assessed how the P wt.% content (from a threshold of 0.02%) negatively affects the mechanical properties of the material, increasing the fragility of the material at higher temperatures. Table 2 provides typical thresholds (maximum allowable wt.%) for Cu, P and Ni.

| Chemical Element | Threshold Scientific Established (Maximum wt.%) |
|------------------|-----------------------------------------------|
| Cu               | 0.10                                          |
| P                | 0.02                                          |
| Ni               | 1.00                                          |

The irradiation embrittlement has been observed for a temperature range from 340 °C to 460 °C, so the experimental limit is relevant according to the reactor operating temperature range, between 290 °C and 350 °C [56]. Other chemical elements in the composition influence the mechanical properties [57] making it necessary to reduce wt.% of pernicious elements at minimum. Specifically, Si and V have more influence on irradiation embrittlement susceptibility.

- Regarding Si, it is necessary to keep the silicon content to a minimum [58] to obtain adequate material toughness, because the presence of silicon influences the ductile–brittle transition temperature ($\Delta RT_{DBT}$) [59].
- Vanadium, V, increases the susceptibility of the material to neutron irradiation embrittlement [60] and decreases the weldability of the steel.

Another element of the alloy that could affect the irradiation embrittlement susceptibility is manganese (Mn): its presence improves the mechanical properties of steels. Consequently, it is usually added in amounts greater than 1% [61] but smaller than 3%. It is important to highlight that the presence of manganese reduces the influence that the material’s manufacturing method (forging or lamination) has on its behavior against neutron irradiation [62]. Mn content is similar between the different standardizations analyzed.

There are numerous databases that show results obtained in the monitoring programs of the mechanical properties of vessel steels, some of them are PR-EDB, IAEA-International Database on RPV Materials, Web-enabled database of JRC-EC, ASTM E 10.02, JEAC4201-2004 and ASTM E900-02 [19]. Likewise, there are numerous standards and material specifications, as well as research papers, technical reports and regulatory guides approved by the Nuclear Regulatory Commission (NRC), the use of which in the selection stage of materials for the vessel is essential to ensure the structural integrity and an adequate mechanical behavior of the material against neutron irradiation.

2.2. Stage 2.—Radiation Damage: Review of the ASTM SPECIAL Publications Dedicated to Radiation Effects on RPV Metals

The increase in brittle–ductile transition temperature with neutron exposure is of considerable importance in the selection of materials for nuclear reactor pressure vessels [63]. In the process of radiation damage, the transfer of neutron energy to the nuclei of solid materials creates lattice defects which modify the properties of these solids, sometimes very significantly [64]. The details of the process vary significantly between different standardized materials and, therefore, must be explored experimentally. The book series entitled “Effects of Radiation on Nuclear Materials” published by the American Society for
Testing of Materials (ASTM) as Special Technical Publications has a rich history, having evolved over the course of five decades starting as a symposium that has provided an international forum for the presentation of current research results, applications studies and open discussions on radiation effects in reactor pressure vessel steels (RPV). Thus, in this work, 20 ASTM STP books related to radiation effects on reactor pressure vessels have been reviewed along with other scientific literature to collect historical conclusions on the materials behavior of the materials specifications most used in the manufacture of RPV.

There are a number of considerations involving experimental details which should be kept in mind when the results of radiation damage experiments are evaluated [35]. A few obvious ones will be discussed below. First, it is important to remember the distinction between an in-pile test and a post-irradiation test. An in-pile test is one in which changes in properties are measured while the material is exposed to a reactor environment similar to the one in which it will eventually perform its design function; a post-irradiation test measures only residual changes which persist after the material is removed from the reactor environment [65]. To determine experimentally the value of the $\Delta RT_{DBT}$ and, therefore, the fracture toughness ($K_{IC}$) of the irradiated material, monitoring capsules (specimens to check the condition of the material in the same service conditions of the vessel) are included in the vessel between the core and the wall. These capsules contain specimens of the vessel material, both welds and thermally affected zone and base material. The surveillance capsules are periodically removed in order to test the specimens, which allows to know in advance the state of the material that makes up the vessel. The capsules include tensile, Charpy impact and fracture toughness specimens, as well as the instrumentation necessary to monitor neutron flux and temperature. Consequently, Figure 4 provides the evolution trend of $K_{IC}$ after irradiation.

![Figure 4. Fracture toughness variation due to irradiation.](image-url)

According to the KTA 3201.2 [66] standard, the damage caused by neutron radiation must be taken into account when the neutron flux ($\phi$) exceeds a value of $1 \times 10^{17}$ n/cm$^2$. In order to quantify the degradation of materials, the monitoring programs according to the KTA 3203 [55] standard require the use of neutron flux intervals ranging from $\phi = 1 \times 10^{18}$ n/cm$^2$ to $\phi = 5 \times 10^{19}$ n/cm$^2$. Thus, Table 3 exhibits the most relevant findings from irradiation experiments on RPV metals using a $\phi$ greater than $1 \times 10^{17}$ n/cm$^2$ according to the KTA 3201.2 requirement [66]. Table 3 provides the main conclusions from the analysis of the most relevant results from ASTM STP irradiation embrittlement experiments. On the other hand, Table 4 reports the most relevant prediction models of ductile-to-brittle transition temperature shift due to irradiation embrittlement.

The first consolidated equation for estimating $\Delta RT_{DBT}$ was established in 1986 by Odette in the ASTM STP-909, being completed by the equation proposed by Miannay in 1990 (ASTM STP 1046). Cu role in embrittlement (and ductile to brittle transition temperature) was identified since the 1950s. Although the NUREG CR 6551 and ASTM E900-02 introduces mainly the influence of P wt.% and a Bias term (in the case of ASTM E900-02) including the irradiation term, differences for usual testing conditions are not very substantial. Figure 5 illustrates the $\Delta RT_{DBT}$ as a function of Cu and Ni wt.% content according to NUREG and E-900-02 models (for an irradiation time, $t_i < 97,000$ h).
| Year | Ref. ASTM | Structural Materials | Testing Conditions | Highlighted Conclusions |
|------|-----------|---------------------|-------------------|-------------------------|
| 1957 | STP-208 [67] | ASTM A-212B | $1.0 \times 10^{19}$ | $60$ | $\Delta (\text{UTS}_{I} - \text{UTS}_{N-I}) = 30.5\%$, $\Delta (\text{Yp}_{I} - \text{Yp}_{N-I}) = 7.7\%$ |
|      |           | ASTMA-302B | $3.7 \times 10^{18}$ | $93$ | $\Delta (\text{UTS}_{I} - \text{UTS}_{N-I}) = 87.2\%$, $\Delta (\text{Yp}_{I} - \text{Yp}_{N-I}) = 29.5\%$ |
| 1962 | STP-341 [68] | ASTM A-212B | $2.10^{18}$ | $240–280$ | $\Delta (\text{UTS}_{I} - \text{UTS}_{N-I}) = 10.9\%$, $\Delta (\text{Yp}_{I} - \text{Yp}_{N-I}) = 4.2\%$ |
| 1967 | STP-426 [69] | ASTM A-212B/302B | $2.10^{18}$ | $25$ | No appreciable changes in the ductile-to-brittle transition temperature. |
|      |           | ASTM A-212B | $9.4 \times 10^{18}$ | $300$ | $\Delta R_{DBT} = 18.33 ^\circ C$. |
|      |           | A302B     | $8.0 \times 10^{18}$ | $260$ | $\Delta (\text{UTS}_{I} - \text{UTS}_{N-I}) = 7.61\%$, $\Delta (\text{Yp}_{I} - \text{Yp}_{N-I}) = 39.74\%$ |
|      |           | A542      | $6.0 \times 10^{18}$ | $180$ | $\Delta (\text{UTS}_{I} - \text{UTS}_{N-I}) = 10.24\%$, $\Delta (\text{Yp}_{I} - \text{Yp}_{N-I}) = 27.52\%$ |
|      |           | A302B     | $3.0 \times 10^{18}$ | $288$ | $\Delta R_{DBT} = 55 ^\circ C$. |
|      |           | A533B     | $5.7 \times 10^{18}$ | $180$ | $\Delta R_{DBT} = 12 – 35 ^\circ C$. |
| 1979 | STP-683 [71] | ASTM A-212B | $1.0 \times 10^{18}$ | $282$ | Embrittlement is maximized at 150 $^\circ C$. |
|      |           | A533B     | $1.0 \times 10^{20}$ | $288$ | $\Delta R_{DBT} = 24 ^\circ C$. |
| 1981 | STP-725 [72] | A533B     | $1.0 \times 10^{19}$ | $290$ | $\Delta R_{DBT} = 27 ^\circ C$. |
|      |           | A533B     | $1.0 \times 10^{20}$ | $280$ | $\Delta R_{DBT} = 7–12 ^\circ C$. |
| 1999 | STP 1325 [75] | A533-B    | $4.0 \times 10^{13}$ | $290$ | $\Delta (\text{Yp}_{I} - \text{Yp}_{N-I}) = 100 \text{ MPa for Cu between 0.5 and 0.9 wt.%}.$ |
|      |           | A533-B    | $4.0 \times 10^{23}$ | $350$ | $\Delta (\text{Yp}_{I} - \text{Yp}_{N-I}) = 180 \text{ MPa for Cu between 0.5 and 0.9 wt.%}.$ |
| 2006 | STP 1475 [76] | A508-2/ A533-B | $10^{19}$ | $282$ | A 508-2: $\Delta R_{DBT} = 11\%$ greater after 209 000 h (24 years) at about 282 $^\circ C$. |

Note: UTS$_{I}$: Ultimate tensile strength before irradiation; UTS$_{N-I}$: Ultimate tensile strength after irradiation; Yp$_{I}$: Yield strength before irradiation; Yp$_{N-I}$: Yield strength after irradiation; $\phi$: neutron flux. Note: irradiation times up to 209,000 h.
Table 4. Review of most relevant prediction models of ductile-to-brittle transition temperature shift due to irradiation embrittlement.

| ASTM Report or Published Standard | Highlighted Contributions |
|-----------------------------------|---------------------------|
| STP-909 (1986) [77]              | Odette presented the equation:  
\[
\Delta R_{DBT} (°C) = 200 \cdot Cu \cdot (1 + 1.38 \cdot \text{erf} (0.3 \cdot Ni / Cu) + 1) \times (1 - \varphi^{0.11})^{1.36} \cdot \varphi^{18} 
\]  
(1) |
| R.G. 1.99 Rev.2 (1988) [78]     | \[
\Delta R_{DBT} = (CF) \times f^{(0.28 - 0.10 \log f)} 
\]  
(2) |
| STP-1046 (1990) [79]            | Miannay presented the equation:  
\[
\Delta R_{DBT} (°C) = 10.98 + 316.4 \cdot (P - 0.008) + 225.29 \cdot (Cu - 0.08) + 12.10 \cdot (Ni - 0.7) + 248.31 \times (Cu - 0.08) \cdot (Ni - 0.7) \cdot \varphi^{0.70} 
\]  
(3) |
| NUREG CR-6551 (1998) [80]       | To obtain the CRP contribution, it is necessary to calculate the \( F(Cu) \) (Equation (6)) and the \( G(\varphi t) \) (Equation (7)) parameters.  
\[
F(Cu) = \{0, Cu \leq Cu_{th}; (Cu - Cu_{th}), Cu > Cu_{th}\} 
\]  
(7) |
| ASTM E900-02 [81]              | \[
\Delta R_{DBT} = SMD + CRP + Bias 
\]  
(9) |

![Diagram of \( \Delta R_{DBT} \) vs. Cu and Ni wt.% content according to NUREG and E-900-02 models.](image)

**Figure 5.** \( \Delta R_{DBT} \) vs. Cu and Ni wt.% content according to NUREG and E-900-02 models.

According to NUREG and E-900-02 models, the \( \Delta R_{DBT} \) is always lower than 40 °C (as established by KTA 3203 [55] while the Cu wt.% is below 0.4% and the Ni wt.% is below 1.2%). This highlights that these theoretical models are less stringent than other experimental work that provides more stringent thresholds [51–54] according to information contained in Table 2.

The nuclear industry is a very conservative sector and, even nowadays, the model most consolidated and used is the U.S. NRC R.G. 1.99 Rev.2 because it is more stringent, meeting even the requirements of experimental works that established chemical composition restrictions for Cu and Ni [48–54]. Thus, Figure 6 provides the acceptable Cu and
The sensitivity to irradiation embrittlement depends on Cu wt.% contents from 0.03 to 0.10 wt.%, as well as on Ni contents for A508-2 and A508-3 and testing $10^{18}$–$10^{20}$ n/cm².

Amayev proposed that $P \geq 0.02$ wt.% negatively affects the mechanical properties of the material. Mager [38] did not find dependence between neutron flux rates from $\phi = 2.5 \times 10^{19}$ n/cm² to $\phi = 8.8 \times 10^{19}$ n/cm².

Odette presented a Cu limitation: 0.10 wt.%.

The NRC draft correlation adds a term representing an additional shift if the steel has been exposed to more than 97,000 h of high temperature.

The A533B steel plate with high content of P exhibited significant hardening, as well as grain boundary P segregation, and a large $\Delta RT_{DBT}$ of 230 °C due to neutron irradiation to a fluence of $6.9 \times 10^{19}$ n/cm² and $E \leq 1$ MeV at 290 °C.

Adequate safety margins of $\Delta RT_{DBT}$ with respect to the German KTA 3201.2. standard curve were observed for all materials with Cu $\leq 0.15$% and Ni $\leq 1.1$% for which the $\Delta RT_{DBT}$ curve is valid.

In ASTM STP 782 in 1982, the first restrictions were proposed; however, Odette in ASM STP 1270, in 1996, established the most consolidated restriction for Cu (0.1% maximum wt.%). Amayev in ASTM STP 1170 (1993) proposed that P content greater than 0.02 wt.% negatively affects the mechanical properties of the material.

3. Results

As the previous review of the historical research on the irradiation embrittlement of RPV ferritic steels stated, to improve materials performance, it is necessary to control the wt.% content of several impurities (Cu, P, V and Si) and the wt.% content of some alloy elements such as Ni. Subsequently, in Section 3.1, an analysis of the evolution of technical restrictions in historical materials used in the RPV construction is performed.
3.1. Stage 3.—Analysis of the Evolution of Chemical Composition Restrictions in Historical Materials Used in RPV Manufacturing

As previously mentioned, in this work, analysis of the main standardized requirements involved in the susceptibility increasing for irradiation embrittlement of the RPV materials used since the first reactors was performed. Table 6 presents the material designation, the chronology of use, the type and generation of reactor, the design code involved in the construction and information on whether Cu, Ni and P were included in the standard.

| Material Code         | Material Type | Chronology       | Type and Generation of Reactor | Design Code       | Cu | Ni | P |
|-----------------------|---------------|------------------|--------------------------------|-------------------|----|----|----|
| ASTM A-302B (plate)   | PWR 1st       | 1960s            |                                | ASME B&PVC        | -  | -  | -  |
| ASTM A-212 B (plate)  | PWR 1st       | 1960s            |                                | -                 | -  | -  | -  |
| ASTM A 543 B (plate)  | PWR 1st       | 1960s            |                                | JSME              | -  | -  | -  |
| JIS G-3120 SQV2A (plate) | 1960s-1980s | PWR 2nd          |                                | KTA               | -  | -  | -  |
| JIS G-3204 SFVQ1A (forging) | 1980s       | PWR 2nd-3rd      |                                | RCC-MR            | -  | -  | -  |
| WWER 15Kh2MFA (forging) | 1970s-1980s | PWR-440          |                                | GT-MHR (General Atomics) | -  | -  | -  |
| WWER 15 × 2MFA (forging) | 1970s-1980s | PWR-440          |                                | ASME B&PVC        | -  | -  | -  |
| WWER 15Kh2MFAA (forging) | 1970s-1980s | PWR-440          |                                | -                 | -  | -  | -  |
| ASME SA-533 Gr. B Cl.1 (plate) | 1980s | PWR 2nd-3rd      |                                | -                 | -  | -  | -  |
| ASME SA-508 Grade 2 (forging) | 1980s | PWR 2nd-3rd      |                                | ASME B&PVC        | -  | -  | -  |
| ASME SA-508 Cl.3 (forging) | 1980s-present | PWR 2nd-4th; PHWR |                                | -                 | -  | -  | -  |
| DIN 20MnMoNi55 (forging) | 1980s-present | PWR 2nd-4th; PBMR |                                | KTA               | -  | -  | -  |
| DIN 22NiMoCr37 (forging) | 1980s-present | PWR 2nd-4th      |                                | RCC-MR            | -  | -  | -  |
| RCC 16MND5 (forging)   | 1980s-present | PWR 2nd-4th      |                                | ASME B&PVC        | -  | -  | -  |
| ASTM A-336 Grade F22V (forging) | (present)  | GT-MHR (General Atomics) |                                | -                 | -  | -  | -  |

Note: PWR: pressurized water reactor; PBMR: pebble bed modular reactor; PHWR: pressurized heavy water reactor; GT-MHR: gas turbine modular helium reactor; WWER: water-cooled water-moderated power reactor. ASME B&PVC: American Society of Mechanical Engineers Boiler & Pressure Vessels Code, KTA-Kerntechnischer Ausschuss (German Nuclear Safety code), RCC-MR: French Nuclear Safety code; JSME: Japanese Society of Mechanical Engineers; Gostgortechnadzor: Russian Nuclear Safety code.

As shown in Table 6, in the earliest steps, no requirements for Cu, Ni and P were included in the standards; in fact, the Cu requirement was not added until the 1970s.

For the analysis, Table 7 presents the main chemical requirements (Cu, P, Ni, Mn, Mo, Si and V) along with the maximum elongation (EL) and the maximum σ_y/UTS ratio (margin of safety against failure by plastic collapse).

Table 7 shows the main chemical and mechanical requirements analyzed in this work.

To study, overall, the evolution of the main requirements involved in the irradiation embrittlement susceptibility (i.e., Cu, P and Ni), Figure 7 reports the change in the maximum allowable wt.% of Cu, Ni and P.

On the other hand, Figure 8 shows the evolution of (Cu, Ni and P) restrictions in wt.% for every origin of standard and technology.

The Si requirements for every generation of materials are very similar. Vanadium increases the susceptibility of the material to neutron irradiation embrittlement (Hawthorne) and it decreases the weldability of the steel. Figure 9 shows the Evolution of V restrictions.

As Figure 9 shows, the most consolidated and novel standardized materials show the minor levels of maximum allowable V wt.%. Thus, the vanadium requirement has been evolving to demand lower maximum wt.% values.

3.2. Stage 4.—Application of R.G. 1.99 to Estimate ∆RT_{DBT} for the Historical and Recent Materials to Analyze the Effect of Requirements’ Evolution

The Regulatory Guide 1.99 Rev.2 proposes the most consolidated model for the calculation of the displacement of the ductile–brittle transition temperature as a function of the Cu and Ni content of the steel and the neutron flux [88]. This model is selected among the models included in Table 4 by Regulatory Guide (R.G.) 1.99 Rev.2 (1988) proposes a model for calculating the ∆RT_{DBT} shift depending on the Cu and Ni content and neutron flux, according to Equation (2) (given in Table 4). Figure 10 exhibits the ∆RT_{DBT} Matrix according to R.G. 1.99 Rev.2 (for neutron fluence of 1·10^{19} n/cm^2) for each analyzed mate-
The maximum allowable $\Delta RT_{DBT}$ established by KTA 3203 [55], 40 °C, is used as an acceptance criterion.

Table 7. Chemical and mechanical requirements of analyzed materials.

| RPV Material                        | Chemical Requirements (Maximum wt.%) | Mechanical Requirements |
|-------------------------------------|--------------------------------------|-------------------------|
|                                     | Cu        | P        | Ni        | Si        | V        | Maximum Elongation (EL) in % | Maximum $\sigma_y$/UTS |
| ASTM A 212B,                        | N.S.      | 0.035    | N.S.      | 0.30      | N.S.      | 23                       | 0.68                   |
| ASTM A 302B                         | N.S.      | N.S.     | N.S.      | 0.40      | N.S.      | 15                      | 0.56                   |
| ASTM A 543 B                        | N.S.      | 0.020    | 4.00      | 0.40      | N.S.      | 18                      | 0.56                   |
| ASME SA 533 Grade B Cl.1            | 0.12      | 0.015    | 0.73      | 0.45      | 0.06      | 18                      | 0.56                   |
| JIS G 3204 SFVQ1A                    | N.S.      | 0.035    | 0.70      | 0.30      | N.S.      | 18                      | 0.56                   |
| ASME SA 508 Grade 2                 | 0.20      | 0.025    | 1.00      | 0.40      | 0.05      | 16                      | 0.64                   |
| DIN 22NiMoCr37                      | 0.11      | 0.025    | 1.00      | 0.35      | 0.05      | 16                      | 0.64                   |
| ASME SA 508 Grade 3;                | 0.20      | 0.025    | 1.00      | 0.40      | 0.05      | 16                      | 0.64                   |
| DIN 20MnMoNi55                      | 0.12      | 0.012    | 0.85      | 0.35      | 0.02      | 19                      | 0.59                   |
| RCC 16 MND5                         | 0.20      | 0.020    | 0–80      | 0.30      | 0.02      | 20                      | 0.66                   |
| JIS G 3204 SFVQ1A                    | N.S.      | 0.025    | 1.00      | 0.40      | 0.05      | 18                      | 0.72                   |
| ASTM A 336 Grade F22V               | 0.20      | 0.015    | 0.25      | 0.10      | 0.35      | 20                      | 0.60                   |
| WWER 15X2MF                         | 0.30      | 0.020    | 0.40      | 0.37      | 0.35      | 14                      | 0.80                   |
| WWER 15Kh2MFA                       | N.S.      | 0.025    | 0.40      | 0.37      | 0.35      | 14                      | 0.80                   |
| WWER 15Kh2MFAA                      | 0.08      | 0.012    | 0.40      | 0.37      | 0.35      | 15                      | 0.81                   |

Figure 7. Evolution of restrictions on Cu, Ni and P wt.% contents.

WWER 15Kh2MFAA (used from the 1970s and 1980s; already in operation) ASME SA-533 Grade B Cl.1 (used in PWR 2nd–4th; already in operation), DIN 20MnMoNi55 and DIN 22NiMoCr37 (used in PWR 2nd–4th) and ASTM A-336 Grade F22V (current designs) provide a $\Delta RT_{DBT}$ shift lower than 40 °C (as established by KTA 3203).

Thus, the most consolidated options—those that show a reliable in-service behavior across decades—had been chosen by establishing more stringent restrictions related to pernicious elements such as Cu, P, Ni or V. In addition, the latest standardized grades incorporated to the design codes have generally used the same conservative criterion, establishing safety thresholds related to the maximum content of the abovementioned alloy elements and impurities, considering, therefore, the most relevant scientific research advances in the field of irradiation embrittlement understanding.
Figure 8. Evolution of restrictions: (a) American standardized RPV materials; (b) German, French, Russian and Japanese standardized RPV materials.

Figure 9. Evolution of vanadium restrictions.

| Cu wt% | 0  | 0.2 | 0.4 | 0.6 | 0.8 | 1   | 1.2 |
|-------|----|-----|-----|-----|-----|-----|-----|
| 0.10  | 5.00 | 14.44 | 18.33 | 18.33 | 19.44 | 19.44 | 19.44 |
| 0.15  | 16.11 | 26.67 | 37.22 | 43.33 | 46.11 | 47.22 | 47.22 |
| 0.20  | 27.78 | 38.89 | 51.67 | 65.00 | 70.56 | 73.89 |     |
| 0.25  | 40.00 | 52.22 | 64.44 | 80.00 | 92.78 | 97.56 | 101.11 |
| 0.30  | 53.89 | 63.33 | 75.00 | 90.00 | 107.22 | 120.56 | 125.00 |
| 0.35  | 67.22 | 75.56 | 86.11 | 100.00 | 116.11 | 133.33 | 147.78 |
| 0.40  | 79.44 | 87.22 | 97.22 | 110.56 | 125.00 |     | 142.22 | 160.00 |

Figure 10. Ductile-to-brittle transition temperature shift ($\Delta RT_{DBT}$) matrix according to R.G. 1.99 Rev.2 (for neutron fluence of $1 \times 10^{19}$ n/cm$^2$).
Elevated maximum elongation is desirable because the material becomes brittle when it is exposed to neutron flux [14]. Whereas, a lower $\sigma_y$/UTS ratio is desirable for seismic resistance, since it implies greater energy absorption capacity before failure. Figure 11 presents $EL$ requirement (%) and $\sigma_y$/UTS ratio as an indicator of the materials toughness (energy absorbed by plastic deformation before break).

![Figure 11](image)

**Figure 11.** (a) Maximum elongation ($EL_{\text{max}}$) requirement (%); (b) $\sigma_y$/UTS ratio as an orientated indicator of the materials toughness (energy absorbed by plastic deformation before break).

Analyzing the trend for elongation and $\sigma_y$/UTS ratio, it is observed that it is the same with respect to the materials evolution. A higher $\sigma_y$/UTS ratio implies that the material absorbs less energy by plastic deformation, whereas a higher $EL$ implies greater ductility. Since a balance between $EL$ and $\sigma_y$/UTS is desirable, a ductility–toughness ratio is defined (Equation (11)).

$$D - T = \frac{EL \times UTS}{\sigma_y}$$

Figure 12 provides the materials that exhibit a most balanced ductility–toughness ratio ($D - T$), showing also the evolution of the ductility requirements (considered an adequate balance between ductility and toughness).

![Ductility increasing for a suitable toughness (balanced behavior)](image)

**Ductility increasing for a suitable toughness (balanced behavior)**

**ASME B&FV code**

- A-508 Gr. 2 (Forging)
- A-533 Gr. B Cl. 1 (Plate)
- DIN 20NiMoCr37 (Forging)
- DIN 20MnMoNi55 (Forging)

**KTA code**

Figure 12. $D - T$ ratio evolution for the materials with a balanced relation between ductility and toughness.

Therefore, more central values are recommendable: i.e., the values exhibited by A-508 Gr. 2, A-533 Gr.B Cl.1, DIN 20NiMoCr37 and DIN 20MnMoNi55, these being the most consolidated standardized materials, developed in the 1980s but still used nowadays. All these specifications are the most consolidated and used in the manufacture of reactor pressure vessels. Therefore, the results confirm the fact that nuclear technology is in constant development, with safety as its fundamental pillar [23,89,90].

The data presented in historical works about the influence of chemical composition, neutron flux and temperature in reactor operating conditions are still considered
valid today, since these results have been verified through the investigation of materials from surveillance capsules removed from reactors that have been in operation for decades [40–43]. Consequently, the analyzed KTA (Germany) and ASME (USA) requirements are more stringent compared with the RCC-MR (France), Gosgortechnadzor and JSME (Japan) codes [91,92].

4. Conclusions

Nuclear energy enables many countries to ensure energy supply security and sustainable development as well as actively addressing environmental challenges. This work is a contribution to keep updated the technical heritage associated with movable and intangible goods related to nuclear power plants, and, to be more precise, the design and manufacturing codes of RPVs and their standardized material specifications which have not been thoroughly studied in scientific and technical literature. The accidents and reactor pressure vessel failures (e.g., Three Mile Island in USA, Chernobyl in Ukraine and Fukushima in Japan) have often caused the establishment of more severe safety specifications containing more stringent technological requirements.

In this work, a novel analysis of the historical modifications and advances in materials properties research and their associated standardized restrictions for RPVs was performed. More than 80 historical research works were analyzed in this study, evaluating the historical conclusions and their impact on design and manufacturing codes and, therefore, on their standardized materials requirements.

The novelty of this new approach lies in the idea of integrating a review and analysis of the historical research results on irradiation embrittlement understanding to evaluate the impact on standards and safety guides. The study is based on a selection of key scientific publications about the influence of chemical composition on the mechanical behavior of materials after irradiation. Thus, the major conclusions resulting from this work are as follows:

- Steels with low levels of impurities are recommended for the current light water RPV steels and for the new-generation nuclear systems. However, it is recommended to review historical scientific advances related to the understanding of radiation embrittlement and the key factors involved in this phenomenon. This review allows one to analyze the evolution of the essential technological requirements and how they were integrated in the codes, standards and standardized specifications. Consequently, this is the rich technical heritage provided by the scientific research and the technical advancement that provides for safe and sustainable nuclear power generation now and in the future.

- According to NUREG and E-900-02 models, the $\Delta RT_{DBT}$ is always lower than 40 °C (as established by KTA 3203 [55]) when the Cu wt.% is below 0.4% and the Ni wt.% is below 1.2%. This highlights that these theoretical models are less stringent than other experimental works that provide more stringent thresholds [51–54], according to information contained in Table 2. The nuclear industry is very conservative and, even nowadays, the model most consolidated and used is the U.S. NRC R.G. 1.99 Rev.2 because it is more stringent, meeting the requirements of several experimental works [51–54].

- The results obtained by applying the analysis based on the consolidated U.S: NRC R.G. 1.99 Rev.2 model allow for the definition of the best material options that correspond to some of the most widely used material specifications, such as WWER 15Kh2MFAA (used from the 1970s and 1980s; already in operation) ASME SA-533 Grade B Cl.1 (used in PWR 2nd–4th; already in operation), DIN 20MnMoNi55 and DIN 22NiMoCr37 (used in PWR 2nd–4th), as well as ASTM A-336 Grade F22V (current designs). This confirms a trend of improving the standards for improving nuclear safety.

- Finally, using a novel ductility–toughness ratio, the materials that exhibit the most balanced ductility–toughness ratio are: SA-508 Gr. 2, SA-533 Gr.B Cl.1, DIN 20NiMoCr37 and DIN 20MnMoNi55.
• Thus, in view of the results obtained, it can be concluded that the best options correspond to recently developed or well-established specifications used in the design of pressurized water reactors. These assessments endorse the fact that nuclear technology is in a state of continual development, with safety being its fundamental pillar.

In the future, new research related to the analysis of technical heritage from the evolution of material requirements for other clean and sustainable power generation technologies will be performed.

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