

Development and Applications of a Specialty Nickel-Based Alloy and the Need for Corrosion Education

Aziz I. Asphahani

Abstract High-performance Nickel-based alloys are proven to be reliable, cost-effective corrosion control measures in many industries (e.g., Chemical/Petrochemical Processing, Pharmaceutical, Oil and Gas, Pollution Control, Energy, . . .). These alloys' resistance to corrosion (uniform, localized and stress cracking) and the role of alloying elements (Cr, Mo, W and Fe) are reviewed. The design concepts of a cost-effective corrosion-resistant alloy are presented in terms of optimum resistance to various forms of degradation, along with test data illustrating its improved resistance to pitting, crevice corrosion and to chloride/H₂S stress cracking and hydrogen embrittlement. The increasing cost of maintenance/downtime, the concerns about the reliability of equipment along with the emphasis on the safety of personnel, the protection of the environment and sustainability are leading to greater awareness about the deleterious impact of corrosion. Design and Process Engineers, along with Maintenance Managers, are entrusted to ensure (from a corrosion perspective) that the "correct" materials selection and corrosion mitigation technologies are implemented upfront, at the design stage. Hence, there is a need for an engineering workforce, educated in the corrosion science fundamentals and trained in the applied corrosion engineering mitigation techniques. Such engineering workforce will be provided through a Bachelor of Science degree in "Corrosion and Reliability Engineering" (the first such degree in the USA) to start in the fall semester of 2010, at the University of Akron. Details are presented on the curriculum development, corrosion content, courses' sequencing and industrial interest/support.

A.I. Asphahani (✉)

Advanced Motion Technologies, Inc., Warrenville, IL, USA

and

"Corrosion Curriculum" Development, The University of Akron, Akron, OH, USA

e-mail: aziz.asphahani@yahoo.com

1 Introduction

For years, nickel-based alloys (e.g., INCONEL¹ and HASTELLOY² alloys) have been relied on to handle corrosive chemicals. While some metals (e.g., Ti, Zr, Ta, Nb) and their alloys offer excellent resistance to several corrosive media, these materials fail to provide the versatility of nickel-based alloys, especially when fluoride ions are present in process streams. Also, many of these metals and their alloys are rather cumbersome in terms of field weld-repairs. In contrast, the nickel-based alloys are well-known for their excellent mechanical properties (strength and ductility), as well as their good welding characteristics, which has augmented their acceptance as the most economical choices for solving severe/chronic corrosion problems.

Conventional corrosion-resistant alloys (e.g., stainless steels) and corrosion protective measures (e.g., coatings, inhibitors) are often selected on the basis of initial low-cost and perceived effectiveness in the intended service. However, the unsatisfactory performance of such conventional approaches is becoming an increased liability to long-term field operations. Recurring maintenance shutdowns and unscheduled downtimes are leading to a greater emphasis on cost reduction, as well as causing real concerns about the reliability of equipment and the safety of personnel. Such emphasis and concerns are the driving force behind the search by corrosion engineers for the correct choice of materials of construction at the design stage. As such, the uniqueness of the nickel-based alloys in providing excellent mechanical properties and corrosion-resistance characteristics is the reason for the increased demand for these high-performance alloys in critical/aggressive services.

It is the purpose of this paper to describe an advanced nickel-based product: Alloy G-50. The factors affecting corrosion and the role of alloying elements are reviewed. Corrosion test results are presented and potential applications in sour gas services are indicated.

In addition, the need for corrosion education is highlighted and information is provided on the first US Bachelor of Science degree in Corrosion Engineering.

2 Alloys Design for Sour Gas Services

The development of alloy G-50 (N06950) was one result of “Mid 1970s” extensive research programs on corrosion resistant alloys (CRA) for sour gas production. The extremely corrosive and toxic deep sour gas wells highlighted issues related to materials reliability and safety of operations [1]. Conventional carbon-steel tubing and other components were rapidly deteriorated by general weight loss, localized

¹ INCONEL is a registered trademark of Special Metals Corporation.

² HASTELLOY is a registered trademark of HAYNES International.

Table 1 Nominal chemical composition (weight percent)

Alloy	Ni	Fe	Cr	Mo	W	Other
718	Bal	19	18	3	–	Nb + Ta = 5
G-3	Bal	19	22	6	–	Cu = 2
625	Bal	3	22	9	–	Nb + Ta = 3
C-276	Bal	3	16	16	4	V = 0.35
G-50	50 min	17	20	9	1	–

Table 2 Hydrogen sulfide stress cracking 5% NaCl + 0.5% acetic acid/saturated H₂S/room temp

Resistant alloys	Yield (ksi)	Threshold (ksi)
718	143	139
G-3	217	213
625	193	189
C-276	218	214
Susceptible alloys		
17-4 PH	125	13
410 SS	90	30

crevice and under-deposit corrosion, stress corrosion cracking and hydrogen embrittlement. Furthermore, the effective use of inhibitors was faced with many limitations.

The inability to effectively inhibit corrosion of conventional steel tubing in deep sour gas production led to the testing of nickel-based CRA products (Table 1 lists the nominal chemical compositions of some of these alloys). In addition to the presence of the highly corrosive H₂S/brines and to bottom-hole temperatures approaching 450°F, the CRA tubular products must possess strength levels capable of handling bottom-hole pressures up to 23,000 psi at depths in excess of 13,000 ft [2, 3]. To meet these extreme stress levels, higher yield strength of CRA tubular products can be achieved by cold working (110–180 ksi), by precipitation strengthening (140–200 ksi) and by cold working plus aging heat treatment (180–280 ksi). Even at strength levels exceeding 140 ksi, the CRA tubular products retained their resistance to various forms of corrosive attack, including H₂S stress cracking [2], and their threshold stresses were much higher than those for stainless steels (Table 2).

While initially the CRA were identified as “inert” in various laboratory tests, further evaluation uncovered the susceptibility of high-strength CRA tubular products to hydrogen embrittlement. This susceptibility was specifically observed for cold worked materials that were heat treated for a few hundred hours at temperatures as low as 400°F (simulating the aging of cold-worked tubes at bottom-hole temperatures). Cathodic hydrogen, produced by direct charging or via galvanic coupling to carbon-steel [4], induced stress cracking of the most corrosion resistant nickel-based alloy C-276, that was cold worked and aged (Table 3).

The least corrosion resistant of the tested nickel-based alloys (containing more iron than alloy C-276 and low to moderate amounts of molybdenum: i.e., alloys 718 and G-3) did not fail in this cathodic hydrogen stress cracking test at room

Table 3 Cathodic hydrogen stress cracking: C-shape specimens (with galvanic coupling to carbon-steel) 5% NaCl+0.5% acetic acid/saturated H₂S/room temp

Alloys	Cold-work (10–60%)	60% cold-work + 200 h at 400°F
718 (19% Fe)	No cracking	No cracking
G-3 (19% Fe)	No cracking	No cracking
625 (3% Fe)	No cracking	Failure
C-276 (3% Fe)	No cracking	Failure

Table 4 Anodic chloride/sulfide stress corrosion cracking: C-shape specimens (no galvanic coupling to carbon-steel) 5% NaCl+0.5% acetic acid/saturated H₂S/400°F

Alloys	Cold-work (10–60%)	60% cold-work + 200 h at 400°F
718 (19% Fe)	Failure	Failure
G-3 (19% Fe)	Failure	Failure
625 (3% Fe)	Failure	Failure
C-276 (3% Fe)	No cracking	No cracking

Table 5 Cathodic hydrogen stress cracking: C-shape specimens (with galvanic coupling to carbon-steel) 5% NaCl+0.5% acetic acid/saturated H₂S/room temp

	Hours to failure	
	C-276	G-50
40% cold-work	NC ^a /NC/NC	NC/NC/NC
40% cold-work + 200 h at 400°F	312/312/816	NC/NC/NC
40% cold-work + 100 h at 932°F	24/24/90	NC/NC/NC

^aNC = No cracking after 1,000 h

temperature. However, when tested at bottom-hole conditions (H₂S plus brines at 400°F) alloys G-3 and 718 failed by anodic stress corrosion cracking, while alloy C-276 did not stress corrosion crack (Table 4). The high-iron containing alloys were extremely susceptible to anodic chloride-sulfide stress corrosion cracking [4, 5]. Furthermore, when evaluating the CRA for resistance to localized attack in chloride environments, alloys G-3 and 718 suffered pitting corrosion [2, 4, 5].

In view of the need for the Ni-Cr-Mo-W system's resistance to localized corrosion and to anodic stress corrosion cracking at bottom-hole conditions (H₂S, Chlorides, Temperatures near 400°F), along with the beneficial effect of iron content in enhancing the nickel-based alloys resistance to cathodic hydrogen stress cracking, the alloy G-50 was formulated to provide an optimum product for sour gas production tubing [6]. The increased iron level to about 17% (compared to less than 5% in alloy C-276) permitted alloy G-50 to better resist the deleterious effect of low temperature aging and cathodic hydrogen stress cracking (Table 5). In addition, the increased nickel content to more than 50% in alloy G-50 favorably improved its resistance to anodic stress corrosion cracking in hot chloride, sulfide and bromide containing environments (Table 6).

Table 6 Anodic stress corrosion cracking: C-shape specimens (exposed 240–1,500 h/400°F)

	825	G-3	G-50	C-276
20% MgCl ₂ (30% cold-work)	2 ^a /2	1/2	NC ^b	NC
% NaCl + 0.5% acetic acid + H ₂ S	2/2	2/2	NC	NC
4.7% ZnBr ₂	2/2	2/2	NC	NC

^a 2/2 = two specimens failed out of two tested specimens^b NC = no cracking**Table 7** Resistance to uniform corrosion in acidizing environments: corrosion rates in mils per year

Temperature (°F)	15% HCl		12%HCl + 3% HF	
	G-3	G-50	G-3	G-50
150	73	55	57	36
200	313	199	689	323
300	20,516	6,896	17,536	8,170

The alloy G-50 (minimum 50% Ni) exhibited resistance to anodic stress corrosion cracking close to that of alloy C-276 and much improved over those of alloy 825 (nominal 41% Ni) and alloy G-3 (nominal 44% Ni). Furthermore, the higher molybdenum content of alloy G-50 (9% Mo compared to 6% Mo in alloy G-3 and 3% Mo in alloy 825) was proven beneficial to improved resistance to localized attack (pitting/crevice and under-deposit corrosion) as well as an essential alloying element to resist uniform corrosion in acidizing environments (Table 7).

The G-50 alloy has been produced in various size tubular destined for the Mobile Bay deep sour gas fields in the USA. Extensive quality control evaluation, based on slow strain rate tests, confirms the reported excellent stress corrosion cracking resistance of this alloy [7]. Such improved corrosion resistance (better than alloys 825, 718 and G-3) along with its moderate cost (lower cost than alloy C-276) are leading to greater interest in alloy G-50 for offshore applications, where seawater and sour services represent tough challenges to the safe and reliable performance of many stainless alloys. Also, the alloy G-50 optimum mechanical properties and ease of weld repairs make it an excellent choice of material as bi-metallic tubing and piping for aggressive sour gas transmission pipelines (thus avoiding the use of inhibitors) and processing equipment.

3 The Need for Corrosion Education

The impact of corrosion on the industrial sectors, the public and daily life is very significant. Corrosion and materials reliability affect industrial complexes, public infrastructures, personnel safety and health, along with severe damages to the environment and sustainable development. The deleterious effects of corrosion are often described in economic terms: as materials degradation/replacement costs and as financial losses. A 2002 report on the “Corrosion Costs and Preventive

Strategies in the USA” calculated the corrosion direct costs to the US economy to be \$ 276 Billion (about 3.2% of the annual GDP).

The report identified technical and organizational barriers to reducing the costs of corrosion and recommended strategies to overcome these barriers (<http://www.corrosioncost.com/preventive/index.htm>). Of the total corrosion cost, 25–30% of the cost is avoidable, if best practices are implemented. Also, it was indicated that savings can be realized through training and corrosion education.

As a follow-up, the importance of corrosion education was highlighted in the 2009 report “Assessment of Corrosion Education” (ACE), by the National Research Council of the US National Academies (http://www.nap.edu/catalog.php?record_id=12560). This ACE report mentioned that among the corrosion prevention strategies, consideration should be given to “improve education and training of staff in recognition and control of corrosion”. Furthermore, the ACE report included a tactical recommendation that the “engineering department in universities should incorporate elective learning outcomes and course work on corrosion into all engineering curricula. Improving the overall awareness of corrosion control will require that more engineers have a basic exposure to corrosion/education”.

It is evident that many engineers recognize that materials degradation and corrosion negatively affect durability and systems integrity. Yet, at the design onset, most efforts are often placed on the materials’ mechanical properties, fabricability, availability and cost. It is believed that the absence of full awareness of the direct costs of corrosion (and its societal impact in terms of safety, health and the environment) may have been the reason for the common neglect, at the design stage, to accurately factor in the belated corrosion damages to many engineered systems and infrastructural components. Eventually, corrosion considerations are then taken into account in more details, ONLY after a first failure case, involving large financial losses along with grave consequences to the public and serious damage to the environment. Hence, there is a need for engineering curricula to include corrosion courses, as well as to emphasize the societal impact of corrosion and to highlight the awareness of its deleterious effects on safety, health and the environment. Such need is best addressed through a comprehensive corrosion engineering education, along with effective corrosion technologists’ training and certification programs.

4 The University of Akron Bachelor of Science Degree in Corrosion and Reliability Engineering

To address the need for corrosion engineering education, the University of Akron-Ohio (with seed money from the US Department of Defense) is establishing a comprehensive baccalaureate program for a corrosion-specific engineering degree through its College of Engineering: the first of its kind in the USA. Also, U. Akron is simultaneously establishing an industry-accredited workforce development

certification course for technical training, through its Summit College (which delivers the U. Akron's 2-year associate degree programs). Housed within the Department of Chemical and Bio-molecular Engineering, the baccalaureate degree in "Corrosion and Reliability Engineering" (CARE) program will be multidisciplinary and will take advantage of the U. Akron's well-known status as a leader in chemical and polymer engineering, as well as being one of the fastest growing colleges of engineering in the USA.

The U. Akron CARE program will be receiving its first-year students in the fall semester of 2010. The program objective is to ensure an effective corrosion education and to address the shortage of qualified corrosion engineers in the USA and around the world. A 2007 NACE survey of its USA members [8], indicated that in the following 10 years it is expected that about 44% of the active "Corrosion Workforce" (engineers and technologists) will retire, without anticipated replacement! In addition, a U. Akron survey (conducted by a market search firm with input from Industry and Associations) evaluated the job prospects for what would be graduates with a bachelor's degree in corrosion engineering. The survey results validated the employment opportunities in a multitude of industrial and governmental sectors for engineers graduating with a "corrosion degree". Also, the survey highlighted the need for effective corrosion engineering education, with 66% of employers perceiving that recent engineering graduates are ill equipped to understand and manage critical corrosion problems. Furthermore, nearly 75% of surveyed managers reported that they had experienced a shortage of qualified job candidates with valid "corrosion skill" sets. In order to ensure an effective corrosion education program and future accreditation, the CARE curriculum development team undertook a systematic approach to the selection and sequencing of the courses and their contents. This approach was based first on identifying the "learning outcomes" that are expected by interested stakeholders as to what future corrosion engineers "must know" and what they should be "able to do" (Table 8). These "learning outcomes" were then incorporated into a sequence of courses that fit within a comprehensive college education. The resulting CARE curriculum stands as a 5-year corrosion engineering degree built on:

- maintaining strong engineering-core,
- ensuring corrosion-centered content,
- emphasizing corrosion management.

The CARE corrosion-centered curriculum is "knowledge-based", through learning the fundamentals of corrosion science and focusing on applied corrosion engineering technologies. Also, this curriculum promotes "skill-based" techniques through apprenticeship models. Furthermore, the CARE curriculum covers various managerial aspects of corrosion problems involving inspection/detection, diagnostic/assessment, prediction and prevention. Such an approach should yield graduating engineers that are capable of addressing issues related to life-cycle costs, fitness for service, future performance/reliability and overall asset management. The corrosion management segment of the CARE curriculum and its learning modules will be developed through collaboration with industrial and interested

Table 8 Stakeholders input on “corrosion engineers”: knowledge/capabilities

“Must know”	“Be able to do”
Industries (Chem. Proc., Oil and Gas, Infrastructure, Energy/Nuclear, Medical, Electronics)	
Corrosion basics/fundamentals	Organize risk-based inspection
Materials selection	Conduct failure analysis
Mechanical properties	Evaluate fitness for service/performance
Chemistry/process environment	Guide maintenance/rehabilitation
Fabrication/manufacturing	Ensure quality control and reliability
Testing/evaluation/standards/specs	Define life-cycle/life-extension/prediction
Government (Department of Defense, Department of Transportation)	
“Knowledge of”	“Ability to do”
Inspection/detection	Prevention
Diagnostics	Assessment
Prognostics	Prediction
Mitigation technologies	Management/optimal design
Maintenance/rehabilitation	Life-extension/materials selection
Expected benefits	
Improved safety	
Cost reduction/asset preservation	
Reduced environmental impact	
Enhanced readiness/productivity	

partners. The educational products will be tested and refined at U. Akron, before being incorporated into the curriculum. The 5-year CARE curriculum also includes industrial work periods in job sectors related to corrosion/materials reliability. Upon graduating, the students will have completed 12 fundamental/“corrosion-centered” courses and 2–4 elective/“corrosion-focused” courses (Table 9).

Overall, this 5-year program will include: 15 basic Science and Math courses, 9 additional engineering courses (Mechanical, Chemical, Electrical and Civil engineering) and typical undergraduate engineering and general education courses, for a total of 136 credit hours (Table 10). Also, the CARE program strategy is to develop modularized instructional materials for use in other engineering curricula/courses and for adaptation to distance learning and outreach/partnership programs.

To ensure applied learning experiences, the corrosion engineering students will participate in co-operative programs to enhance their education. These co-op students will be immersed in a couple of full-time, semester-long work periods with the same company, each time with increasing level of responsibility and trust. The students are to be personally mentored by industrial professionals and will become an integral part of the company team. The interpersonal connections will serve as motivation for success on the job, which is reflected back in the classroom. The co-op students will demonstrate greater self-esteem, more confidence in their abilities, and a deeper understanding of the connections between fundamentals taught in the classroom and their application on the job.

Table 9 Listing of corrosion-centered courses and some elective courses

Fundamentals/“corrosion-centered” courses	
Laboratory tools for corrosion engineers	
Materials science for corrosion engineers	
Materials and energy balance for corrosion engineers	
Fundamentals of aqueous corrosion	
Corrosion lab/electrochemistry	
Prevention of aqueous corrosion	
Aqueous corrosion lab/protection technologies	
Fundamentals of Hi-temp/gaseous corrosion	
Prevention of Hi-temp/gaseous corrosion	
Hi-temp/gaseous corrosion lab/protection technologies	
Corrosion management-I (diagnostic, prognostic, mitigation)	
Corrosion management-II (life-cycle costing, optimal design)	
Electives/“corrosion-focused” courses	
Risk-based inspections	
Corrosion in the chemical processing industries	
Refinery and petro-chemical processing corrosion	
Oil and gas/pipeline integrity	
Cathodic protection and anodic protection	
Metallic coatings/electroplating	
Organic coatings/polymers	
Infrastructures/bridges life-extension	
Reliability/systems integrity	
Sensors/condition-based inspections	
Failure modes and effects analysis	
Microbiologically induced corrosion	
Bio-materials/medical implants	
Safety, health and corrosion	
Environmental sustainability and corrosion	

Table 10 Overall courses:
corrosion and reliability
engineering B.S. degree

Fundamentals/“corrosion-centered” courses	12
Electives/“corrosion-focused” courses	4
Basics/“engineering-core” (Math and Sci) courses	15
Other engineering (Chem., Mech., Elec., Civil) courses	9
General education courses	10
Total	50 courses ^a

^a 5-Year program (136 Credit Hours)

The CARE students will also be engaged in their prospective fields through participation in numerous U. Akron’s student design teams that compete in regional, national and international student competitions. These activities, combined with a required capstone design project for all seniors, ensure that students graduate with hands-on experience in applying engineering principles to real world problems and

with an understanding of the skills that are critical to project management (e.g., scheduling, budgeting, time management, teamwork, communication).

The educational aspects of the U. Akron CARE program are crucial to continuing success in mitigating corrosion and, in the longer term, are likely to have the greatest positive impact for increased reliability and safety of engineered systems. Also, this program is poised to provide the next generation of corrosion experts and to develop education and training tools for a broader range of engineers, managers and policy makers. Furthermore, the CARE program addresses the goal of creating a “pipeline” of baccalaureate-level engineering graduates who will understand the impact of corrosion-related decisions in the early design stages and who are well trained to conduct valid analyses of materials selection and corrosion-protection measures, in order to ensure reliability and life-cycle cost effectiveness.

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