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The History of Corrosion Protection

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The works of Plato (427–347 B.C.) contained the first written description of corrosion. Plato defined rust as the earthy component separating out of the metal. Georgius Agricola held to the same opinion some 2000 years later in his great mineralogical work *De natura fossilium*: "Iron rust (lat. ferrugo or rubigo) is, so to speak, a secretion of metallic iron. Iron can be protected against this defect by various wrappings, such as red lead, white lead, gypsum, bitumen or tar." Gaius Secundus Pliny also mentioned bitumen, pitch, white lead, and gypsum as protecting iron and bronze against corrosion. He reported that Alexander the Great had constructed a pontoon bridge at Zeugmar on the Euphrates with the aid of an iron chain. Links that were inserted later suffered rust attacks, while the original ones remained immune. The opinion, sometimes expressed today, that modern iron is inferior and more corrosion-prone than old iron, was thus current even in ancient times [1].

The concept of the *corrosion* process, derived from the Latin *corrodere* (to eat away, to destroy), first appeared in the *Philosophical Transactions* in 1667 [2]. It was discussed in a German translation from the French on the manufacture of white lead in 1785 and was mentioned in 1836 in the translation of an English paper by Davy on the cathodic protection of iron in seawater [3]. However, almost until the present day, the term was used indiscriminately for *corrosion reaction*, *corrosion effects*, and *corrosion damage*. Only in DIN* 50900, Part I, were these terms distinguished and defined [4] (see Section 2.1).

1.1 Corrosion Protection for Buried Pipelines

The active and passive electrochemical processes on which present-day corrosion protection is based were already known in the 19th century, but reliable protection for pipelines only developed at the turn of the 20th century.

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* All cable references contained in this text are based upon cable specifications in Germany as required by DIN (Deutsche Industrie Normen). We are aware that these specifications may or may not be applicable to the reader's specific requirements, and we therefore recommend the reader consult local standards and codes to ensure compliance with the necessary local codes. Some of the cables are defined in a list of American and European electrical cable sizes located in the front of this book.

Corrosion protection using bitumen coatings reaches back into antiquity. The most ancient occurrence of bitumen deposits was in Mesopotamia. Many writers of antiquity, such as Dido, Strabo, and Vitruvius, mention that asphalt was obtained for many years near Babylon. About 5000 years ago, the streets of Ur, capital of the Sumerians (north of present-day Kuwait), were lit at night with mineral oil. Natural gas was reported to be used for lighting in the Middle East and China.

Bitumen was used in ancient times as an adhesive for sealing hydraulic structures and as mortar for masonry [5]. The Bible mentions that Noah used pitch for caulking the Ark. Not unlike the Tower of Babylon, the houses of one of the most ancient cities in the world, Mohenjo-Daro in the upper Indus valley, were constructed with bricks of clay and bitumen mortar [6].

The earliest metal pipelines, made of copper, bronze, and lead, had no protection against corrosion. The pipes were often surrounded by lime and gypsum mortar for sealing, cohesion, and protection. These early metal pipes are rarely found today because the valuable metals were reused once the pipelines were abandoned. In 1907 the archaeologist Borchardt found the earliest metal pipe at a temple complex near the pyramid of King Sahu-re. It was part of a 250-m-long pipeline which was used to carry rain water from the temple courtyard. The 1-m-long sections, with a diameter of 47 mm, were made of 1.4-mm-thick beaten copper, curved, and the overlapping longitudinal edges hammered together. The pipes were set into a rock-hewn channel and covered with lime mortar. The only well-preserved pipe in its bedding is shown in Fig. 1-1. Its age can be taken as 4500 years since records indicate that King Sahu-re belonged to the fifth dynasty of Egyptian rulers [7].

The Phoenicians were building water ducts and pipelines of clay, stone, or bronze about 1000 B.C. and the construction of long-distance water pipelines flourished in imperial Roman times. The water supply lines of Rome had a total length of about 450 km, and consisted mainly of open or covered water ducts. The Roman writer Vitruvius gives a fairly accurate description of the manufacture of lead pipes [8]. The pipes were above ground and were often laid beside the roadway or in ducts inside houses [9].

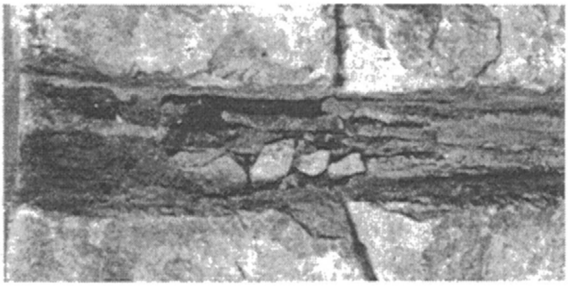


Fig. 1-1 The world's oldest metal pipe from the temple of King Sahu-re (photo: Staatliches Museum, Berlin).

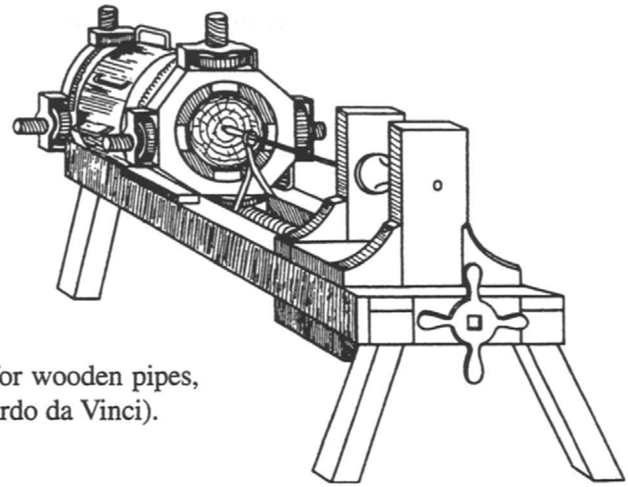


Fig. 1-2 Drilling machine for wooden pipes, about 1500 (sketch by Leonardo da Vinci).

With the fall of the Roman Empire, the ancient water supplies petered out. In early medieval times, people were content to conduct local water in wooden pipes to public cisterns. The first wooden pipelines for water were laid at Lübeck about 1293 and in 1365 at Nuremberg. In 1412 the Augsburg master builder Leopold Karg first used wrought-iron pipes in conjunction with wooden pipes to supply water. Because of their propensity to corrosion, they seem to have proved a failure and a few years later they were exchanged for wooden, lead, and cast-iron pipes.

The author of the first German natural history, *puoch von der Natur*, Chunrad von Megenberg, reported in 1349 that mainly larch and fir were used for water supply [11]. The trunks were often steeped in lime water or brine before they were bored through on a drilling machine like the one sketched by Leonardo da Vinci (Fig. 1-2). Wooden pipes with one end tapered and the other socketed were wedged into each other. Pipes with abutting ends were held together by wrought-iron ferrules (called "Tuchel" ferrules). Figure 1-3 shows wooden pipes with a cast-iron ring ferrule (laid before 1760). The sleeves were sealed with hemp, tallow, pitch, wax or resin, which also acted as protection for the iron rings. It is recorded that wooden pipes were painted with pitch or tar. Later on, wooden pipes with an internal coating of liquid tar were used in London and New York for town and natural

Fig. 1-3 Oak water pipe over 200 years old laid above ground in the Wadgassen Abbey (Saarland) with cast iron clamps (photo: Mannesmann Archives).

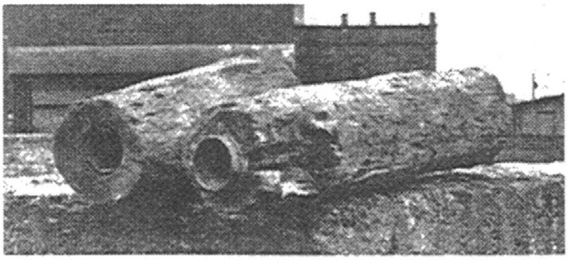


Table 1-1 Evolution of ferrous metals technology and corrosion protection

Year	4000	2000	0	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
Age	Prehistoric and early days	Ancient times		Middle Ages					Age of rationalism			Modern Age		
Period of culture	Early Stone Age	Bronze Age	Iron Age										Plastics	
Raw materials and fuels	Meteoric iron	Iron ore and charcoal										Hard coal, coke	Natural gas	
Source of energy	Wind	Physical strength		Water power								Heat energy	Atomic energy	
Smelting and production of wrought iron		Charcoal hearth and iron foundry (direct reduction from ore)			Blast furnace (indirect production of pig iron)									
Process for the production of wrought iron		Renn process			Oxidation							Puddling	Bessemer, Siemens and LD converter, open hearth	
Type of iron	Native iron	Weldable wrought iron and steel								Cast iron in Europe		Mild iron, steel and ductile cast iron		
Importance of iron	Disappearing	Predomination of bronze	Iron is generally used for the production of apparatus and weapons, wood is an important construction material besides stone									Most important construction material for machines, bridges, vehicles, ships		
Corrosion protection	Bitumen		Burnishing		Paint coatings				Metallic coatings		Tar	Thick organic coatings	Cathodic protection	
Binder	Wax, bitumen, varnish		Pitch and resins		Asphalt lacquer, linseed oil, shellac					Turpentine oil			Synthetic resins	
Pigments	Iron oxide, ochre, gypsum, chalk			Red lead, cinnabar							White lead	Ferric oxide, zinc dust		

gas. The protection of wooden pipes against rot may be regarded as the precursor of corrosion protection of wrought-iron pipelines.

The Bavarian Duke Maximilian I commissioned the master builder Simon Reifenstuel in 1618 to lay the first pipeline for brine from Reichenhall to Traunstein. The 31-km-long line required 9000 wooden pipes. Two centuries later the King of Bavaria commissioned the extension of the pipeline from Reichenhall to Berchtesgaden. The noted Karlsruhe engineer, George Friedrich von Reichenbach, had iron pipes cast to his own specification for this first German high-pressure pipeline. The initially porous cast pipes had to be sealed with a mixture of linseed oil and finely ground quicklime to enable them to withstand a pressure of 43 atmospheres [12]. This treatment with linseed oil was apparently not intended to be a protection against internal corrosion, which was known by the end of the 17th century. So-called "calcination" of pipelines was understood to include not only the formation of iron rust nodules with wastage of pipelines but also internal corrosive attack.

It cannot be ascertained with accuracy when molten iron was first obtained in the European cultural sphere. The forge production of iron in Siegerland goes back to Roman times. Iron was made in the ancient world using charcoal-burning forges and only a small portion was converted into steel for weapons (see Table 1-1). Only in medieval times, when water wheels supplied the required air, were the temperatures necessary for iron smelting reached. We can assume that the first cast iron was obtained in Europe in about the year 1380 but a few decades elapsed before cast-iron pipes for water supply could be made, the impetus being given by the casting of gun barrels. The Master Christian Slanterer cast 30 small breech loaders in Siegen in 1445. Twelve years later Count Johann IV required a water supply for Dillenburg castle and the order for cast-iron pipes went to the same master. Figure 1-4 shows the socketed ends of a well-preserved pipe, 1.1 m long by 70 mm in diameter, with lead-sealed sleeves [13].

Forged and cast-iron pipes were painted with molten pitch or wood tar at the close of medieval times. A work in 1827 states that pipes had been protected by coal tar for a long time [14]. Before being buried, in 1847 cast-iron gas and water pipes were treated with tar in Hanover. In Germany the tarring of wooden roofs was known before 1770. Coal tar had been produced in quantity during production of lighting gas between 1792 and 1802 in England. William Murdoch constructed the first gas production plant in Soho and illuminated the factory of Boulton and Watt on the occasion of the peace of Amiens in 1802.

Cast-iron pipes were used for the mains in the early stages of town gas supply, their sockets being sealed with tarred rope, oakum, or lead. Originally the connection pipes were lead and later of galvanized or coal-tarred forged iron. After the defeat of Napoleon in 1815, there was a surplus of cheap musket barrels, and these

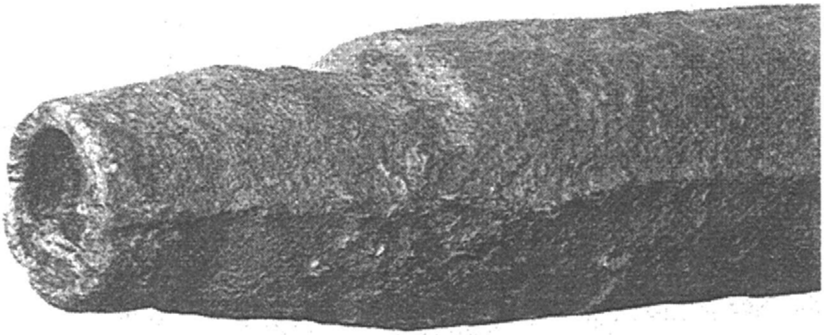


Fig. 1-4 End socket of a cast-iron waterpipe sealed with lead laid in 1457 (photo: Rheinstahl, Gelsenkirchen).

were often used as house connections for town gas pipes. The term "barrel" is still used in England to describe gas connection pipes [15].

The Dresden and Leipzig gasworks were founded in 1828 and the red lead putty socket seals were changed to seals of tarred rope when considerable losses were experienced in the grid. An outer varnish coating was applied as corrosion protection for pipes and connections. The *Leipziger Regulator* of 1863 stresses external protection against destruction by oxidation in its instruction for safe pipelaying. In England between 1830 and 1850 we find directions on the use of coal tar and asphalt tar together with other materials for pipe protection. An English company founded in 1884 for the manufacture of asphalt tar and mastic cladding was the first to use mineral filling materials.

After 1860 in the United States, water mains were only occasionally given coatings of tar. About 1896 the activities of English undertakings were extended to America, where chiefly bare metal pipelines had previously been laid. Water supply pipes were coated internally with bitumen in America after 1912. Vicat (1837) in France and J. Bull (1843) in America introduced the widely known cement mortar as a protective material for water pipes [16].

The best-known English pipe protection material was invented by Angus Smith, and consisted of a mixture of coal tar and linseed oil. Occasionally pipes were laid in sand or pitch-filled wooden ducts to protect them against especially aggressive soils. Bitumenized paper-wrapped pipes for gas lines that could withstand pressures of 20 atmospheres were first shown during the Paris Exhibition in 1867 though they had come into use for water supply shortly before then (Fig. 1-5). Zinc plating was reported to be an effective protection for wrought-iron pipes in 1864. F. Fischer mentioned cathodic protection for the first time in an exhaustive report. In 1875 there was a report on the use of mineral wool as insulation and of tarred or asphalted

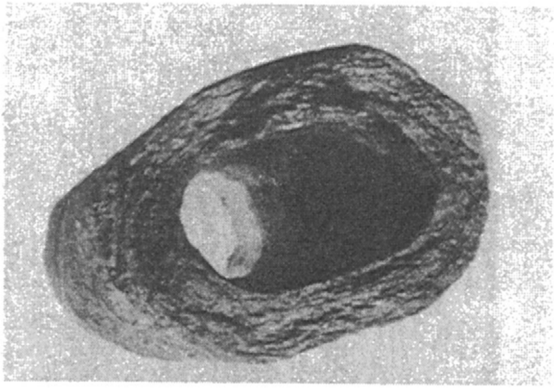


Fig. 1-5 Asphalt paper pipe from a well water pipeline laid in Crailsheim in 1863.

pipes. The first warning of the destruction of gas pipes by aggressive soils and stray currents dates from 1892.

Jute, soaked in molten coal tar pitch, was used after 1900 when it was found desirable to provide forged pipes with a thicker coating. After the First World War, this was further improved with mineral bitumen and a mixture of slate and lime powder or with powdered granite. The change from the use of tar to oxidized bitumen with much improved physical properties made possible the deposition of thick layers inside the water pipes. Wool felt was introduced at the end of the 1920s to eliminate the rot experienced with soaked jute, resulting in a considerable improvement in cladding quality. Figure 1-6 shows the application of bitumenized wool felt at a pipe works which achieved considerable improvement in the quality of the coating. A prognosis, repeated in the journal *Gas- und Wasserfach*, "that the external protection in its present form will not permit attack on pipes," proved to be too optimistic. Since 1953 pipe works have changed from wool felt to glass wool as a support material for bitumen for general use, mainly for mechanical reasons [17].

Field coating of welds has always presented problems. Straw and jute with a greasy material was employed in 1910, but this later saponified in the soil. By chance the pharmacist Schade of Berlin learned of this problem and recommended the use of petroleum jelly in a bandage-like application. Hot-applied bitumen bands, as used by pipe works since 1928, proved to be most durable. Since 1930, electrical measuring methods have played an important part in research into insulation bands and pipe coverings carried out by the Gas Institute in Karlsruhe, the present-day Engler-Bunte Institute [18].

As production increased, new coating materials for pipe protection evolved and a variety of synthetic materials became available. In 1950, continuous-laid pipelines in America and Italy were coated with polyvinyl chloride tapes applied

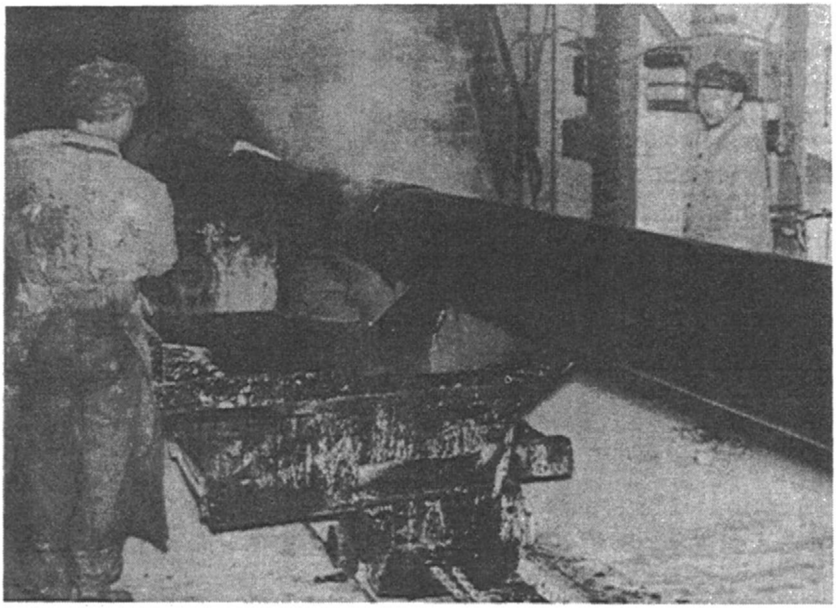


Fig. 1-6 Coating of a line pipe with bitumen in the pipemill in 1935 (photo: Deutsche Röhrenwerke, Düsseldorf).

by wrapping machines, but even multiple layers gave inadequate protection against mechanical damage. Better results were achieved from 1960 onward with a direct-ring, nozzle-extruded, polyethylene tube that was shrunk onto the pipe with the addition of an adhesive. A process was developed for large pipes by melting polyethylene powder onto the rotating preheated pipe [19]. In Germany, polyethylene coating is carried out and tested according to DIN 30670 [20]. Subsequent coating on the construction site is usually with plastic tapes according to DIN 30672 [21].

1.2 Corrosion Protection by Painting

Ancient iron structures sometimes show no sign of corrosion or at most, very little. The clean atmosphere of past centuries may be responsible in that it allowed a very thin adherent layer of oxide to develop on the surface [22]. This layer very often protects against even today's increasingly aggressive industrial pollutants. Very often the conditions of the initial corrosion are the ones that determine the lifespan of metals [23]. A well-known example is the sacred pillar of Kutub in Delhi, which was hand forged from large iron blooms in 410 A.D. In the pure dry air, the pillar remains free of rust traces but shows pitting corrosion of the iron buried in the soil. However, a sample of this 99.7% pure iron brought to England corroded as fast as any other forged iron.

In Europe and India, iron blooms were made in small smelting furnaces using charcoal and air supplied by bellows; a single smelting yielded only 8 to 10 kilos of forged iron. The development of iron was different in China. The Chinese used anthracite as early as 200 B.C., and this enabled them to make cast iron mainly for utility purposes, e.g., ploughshares, cauldrons, or large vases. The technique of iron casting reached Europe only toward the end of the 14th century. Table 1-1 reviews the development of iron manufacturing technology and of corrosion [24] protection [25]-[28].

The necessity to protect steel and iron against corrosion was generally recognized during the 18th century [14]. The first modern reports on rust-protective paints appeared in 1822 in *Dinglers Polytechnischem Journal.* They proposed to use varnish, resin or vegetable oils for painting steel surfaces. The basic essential of good painting technique, the thorough cleaning of metallic surfaces before painting, seems to have been recognized by 1847. Red lead as a primary coating was recommended in 1885 [14]. Paints and varnishes made from coal tar were used in America after about 1860 to protect iron and steel in shipbuilding, but originally were used only for coating the interior surfaces of iron ships. Coal tar paint was first used in 1892 to paint a large floating dock. The locks, floodgates, and weirs of the Panama Canal were sprayed with tar paint in 1912.

A frequently cited example of protection from atmospheric corrosion is the Eiffel Tower. The narrow and, for that age, thin sections required a good priming of red lead for protection against corrosion. The top coat was linseed oil with white lead, and later coatings of ochre, iron oxide, and micaceous iron oxide were added. Since its construction the coating has been renewed several times [29]. Modern atmospheric corrosion protection uses quick-drying nitrocellulose, synthetic resins, and reaction resins (two-component mixes). The chemist Leo Baekeland discovered the synthetic material named after him, Bakelite, in 1907. Three years later the first synthetic resin (phenol formaldehyde) proved itself in a protective paint. A new materials era had dawned.

1.3 History of Cathodic Protection

In 1936, at Khuyut Rabuah near Baghdad, several clay jugs about 14 cm high were found. Inside was a narrow, pitch-sealed copper cylinder, containing a corroded iron kernel. Similar jugs were found in the ruins of Seleucis on the opposite bank of the Tigris. The assumption is that these objects originate from imperial Roman times (27 B.C. to 395 A.D.) and Wilhelm König, a past director of the Baghdad antiquities administration, believes that these objects are battery cells used for gilding small pieces of jewelry by electrolytic processes. He writes: "All these finds may prove that galvanic electricity was known a long time before Galvani (after whom it was named) experimented with frogs' legs (1789)" [30].

The attraction of rubbed amber and some other effects of electricity were known in ancient times. We know from finding nails in an old wreck that the Romans knew about contact corrosion combined with electric current flow. A skin of lead as a protection against boring worms covered the wooden planks of the ship and was nailed down with copper nails. Galvanic couples formed between the lead and the copper nails and the less noble lead sheets around the nails corroded in the seawater and fell off. The shipbuilders discovered a simple solution and covered the heads of the copper nails with lead as well. Galvanic current flow between the two metals was eliminated and corrosion was prevented [26].

It is not certain whether Sir Humphrey Davy (Fig. 1-7) knew of these considerations. He accepted a commission from the Admiralty for the protection of copper-clad wooden ships, which had been introduced in 1761. During his numerous laboratory experiments, he discovered the cathodic protection of copper by zinc or iron [3]. Davy had already put forward the hypothesis in 1812 that chemical and electrical changes are identical or at least arise from the same material property. He believed that chemical reaction forces could be reduced or increased by altering the electric state of the material. Materials can combine only if they have different electric charges. If an originally positive material can be artificially negatively

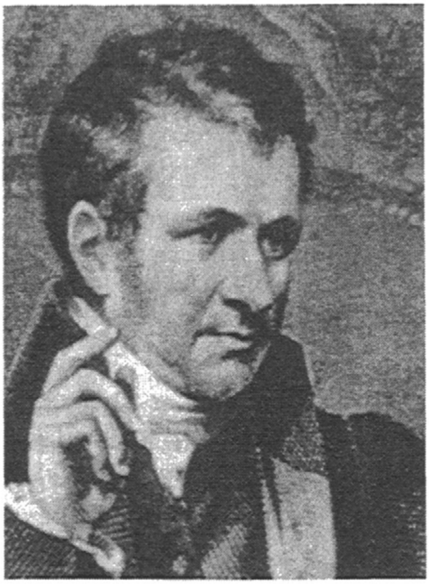


Fig. 1-7 Sir Humphrey Davy.

charged, the binding forces are destroyed and can no longer participate in corrosion reactions.

The beginnings of galvanic electricity and investigations on electrolytes were based on Galvani's experiments with frogs' legs in 1789. The Italian physicist Alessandro Volta discovered in Pavia in 1797 the so-called voltaic pillar. For the first time current was produced from an electric cell. The reverse process, electrolysis, had been discovered by Alexander von Humboldt in 1795 in an electrolytic cell with zinc and silver electrodes in an aqueous electrolyte. In 1798 Ritter noticed that the potential series of metals was identical with the ranking of metals according to their oxidizability.

Although these discoveries can hardly be called electrochemical, the explanations given by Davy are remarkable. Davy had established that copper was a metal which acted weakly positive in a galvanic potential series. He deduced from that, that the corrosive action of seawater on copper could be prevented if it were weakly negatively charged. If the copper surface became negative (i.e., a cathode) then all chemical reactions, including corrosion, would be prevented. To explain the process, Davy performed experiments in which polished copper coupons were immersed in weakly acidified seawater. A piece of tin was soldered onto one of the copper coupons. After 3 days the copper coupons without tin showed considerable corrosion whereas the specimen with the soldered tin bore no trace of any corrosion. Davy came to the conclusion that other non-noble metals such as zinc or iron could provide corrosion protection. Davy carried out further experiments with the help of his pupil Michael Faraday. From this work it became apparent that the location of the zinc was immaterial. On another copper coupon to which an iron coupon was soldered, and which was then connected to a piece of zinc, not only the copper but also the iron was protected against corrosion.

After Davy communicated these results to the Royal Society and the British Admiralty, he obtained permission in 1824 to begin practical experiments on the copper cladding of warships. These experiments were carried out at the Portsmouth naval base. Davy attached zinc and cast-iron plates to the copper-clad ships to protect against corrosion. He established that cast-iron was the most economical material. Cast-iron plates 5 cm thick and 60 cm long gave very satisfactory results on nine ships. On ships' hulls where rivets and nails were already rusted, the corrosion protection was only effective in the immediate vicinity of the anodes. To explain this, Davy carried out further experiments on the warship *Sammarang* (Fig. 1-8). The ship had been covered with new copper sheet in India in 1821. Cast-iron metal plates constituting 1.2% of the total copper surface of the ship's hull were fixed to the bow and the stern. The ship then made a voyage to Nova Scotia (Canada) and returned in January 1825. Apart from some attack at the stern which was attributed to water vortices, there was no corrosion damage to the rest of the ship. Equally good results were achieved with the Earl of Darnley's yacht *Elizabeth* and the 650-ton

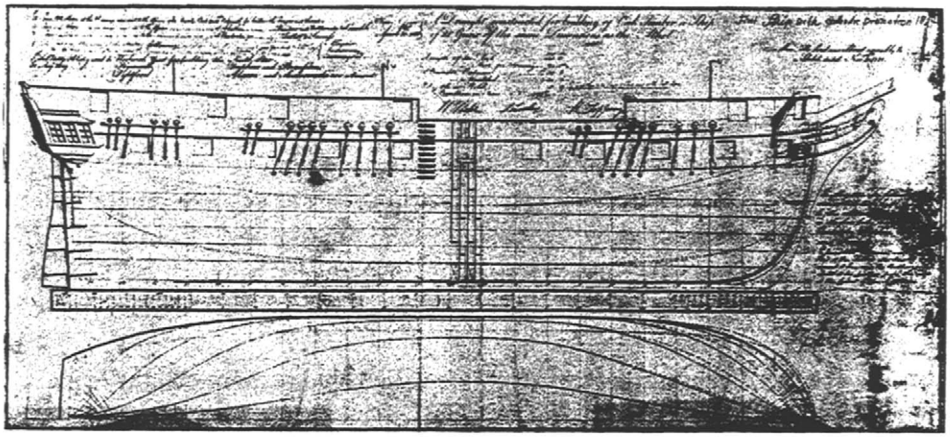


Fig. 1-8 Constructional drawing of the *Sammarang*, which was the first ship to make a sea voyage to Nova Scotia from March 1824 to January 1825 with cathodic protection of the copper sheathing.

freighter *Carnebra Castle*. Each ship was equipped on the stern and bow with two zinc plates amounting to 1% of the copper surface. The copper cladding looked as good as new after the freighter returned from Calcutta.

Some years after Davy's death, Faraday examined the corrosion of cast iron in sea water and found that it corrodes faster near the water surface than deeper down. In 1834 he discovered the quantitative connection between corrosion weight loss and electric current. With this discovery he laid the scientific foundation of electrolysis and the principles of cathodic protection.

Apparently without knowledge of Davy's experiments, the inspector of telegraphs in Germany, C. Frischen, reported to a meeting of the Architekten-und Ingenieur-Verein at Hanover in 1856 the results of a wider experimental enquiry, over a long period, "with particular regard to the protection of the most important and widely used metal, wrought iron, which constitutes the most important parts of the large structures, like bridges, locks, gates, etc." Frischen soldered or screwed pieces of zinc onto iron as a protection against seawater and concluded "that an effective protection of iron is doubtless due to the influence of galvanic electricity." However, achieving a successful and practical protective technique would have required many protracted, large-scale experiments [31] and [32].

It is little known that Thomas Alva Edison tried to achieve cathodic protection of ships with impressed current in 1890; however, the sources of current and anodic materials available to him were inadequate. In 1902, K. Cohen achieved practical cathodic protection using impressed direct current. The manager of urban works at

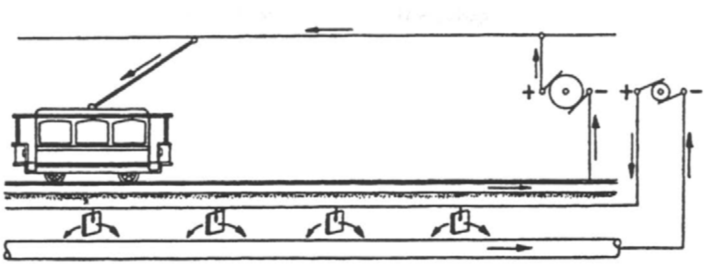
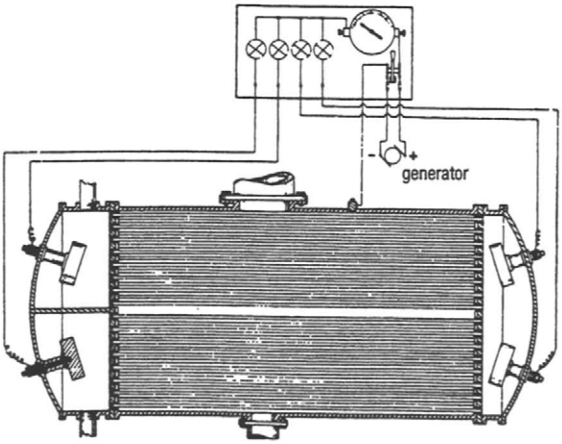


Fig. 1-9 Diagram of cathodic protection from the patent of H. Geppert of (DRP No. 211612).

Karlsruhe, Herbert Geppert, constructed the first cathodic protection installation for pipelines in 1906. This was a direct current generator of 10 V 12 A capacity protecting 300 m of gas and water pipelines within the electrical field of a tramline [33]. Figure 1-9 shows the principle for which H. Geppert obtained a German patent in 1908 [34]. Protection using consumable anodes was termed "electrochemical protection" at a Congress of the Institute of Metals in Geneva in the autumn of 1913.

To protect steam boilers and their tubes from corrosion, E. Cumberland used cathodic impressed current in America in 1905. Figure 1-10 has been taken from the corresponding German patent [35]. In 1924 several locomotives of the Chicago Railroad Company were provided with cathodic protection to prevent boiler corrosion. Where previously the heating tubes of steam boilers had to be renewed every 9 months, "the costs fell sharply after the introduction of the electrolytic

Fig. 1-10 Internal cathodic protection from the patent of E.G. Cumberland of (DRP No. 247544).



process." Aluminum anodes with applied dc were used by A. Guldager in Denmark for internal protection of hot water supply plants. Cathodic protection was thereby provided to the interior of the warm water tank and the connecting pipes by formation of a secondary surface film.

At the beginning of the 20th century, with the development of stainless steels, the passivity of metals became technically important in corrosion protection. In a presentation at the international exhibition of chemical engineering (ACHEMA) in Frankfurt in 1958, it was asserted that it was thanks to metal passivity that progress from the Stone Age to the age of metal technology had been possible [36]. Investigation of passivity phenomena in the 1930s and particularly after the Second World War led to electrochemical investigations and the knowledge that potential was an important variable in corrosion reactions. Great progress in measuring techniques occurred with the development of the potentiostat in the 1950s and systematic investigation of the dependence of corrosion parameters on potential began worldwide. The scientific basis for general electrochemical protection was laid. By determining the limiting potentials for the occurrence of certain corrosion phenomena, in particular local corrosion such as pitting and stress corrosion [37], this work led to the concept of protection potentials.

The passivating stainless steels presented a possibility for developing anodic protection. High-alloy steels, similar to carbon steels, are not capable of being cathodically protected in strong acids because hydrogen evolution prevents the necessary drop in potential. However, high-alloy steels can be passivated and maintained in the passive state by anodic protection. C. Edeleanu was the first to demonstrate in 1950 that anodic polarization of the pump housing and connecting pipework could protect a chromium-nickel steel pumping system against attack by concentrated sulfuric acid [38]. The unexpectedly wide range of anodic protection is due to the high polarization resistance of the passivated steel. Locke and Sudbury [39] investigated different metal/medium systems in which the application of anodic protection was relevant. Several anodically protected installations were in operation in the United States by 1960, e.g., storage tanks and reaction vessels for sulfonating and neutralization plants. Not only did the installations have a longer life but also a greater purity of the products was achieved. In 1961 anodic protection was first applied on a large scale to prevent stress corrosion cracking in a caustic soda electrolysis plant in Aswan [40]. Anodic protection for caustic soda tanks has been used on a large scale since the end of the 1960s and electrochemical corrosion protection methods have become of permanent importance for industrial plants (see Chapter 21).

During the previous century, the success of cathodic protection was often a matter of chance. In 1906 at the instigation of the DVGW,[1] F. Haber and L. Gold-

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[1] The Deutscher Verein des Gas- und Wasserfachs, the current name of an earlier association of gas and waterworks engineers.

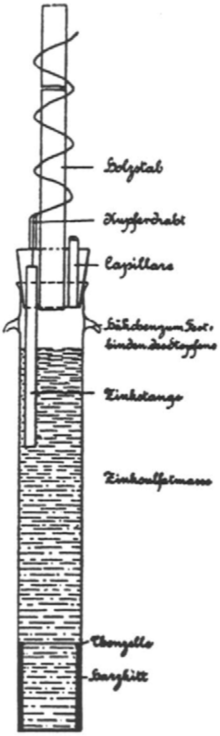

Fig. 1-11 Nonpolarizable Zn/ZnSO$_4$ electrode developed by Professor Haber in 1908.

schmidt studied the scientific fundamentals of cathodic protection. They recognized cathodic protection and stray current corrosion as electrochemical phenomena and Haber's well-known circuit for measuring current density, soil density, soil resistance, and pipe/soil potentials is described in the *Zeitschrift für Elektrochemie* [41]. Haber used nonpolarized zinc sulfate electrodes to measure potential (see Fig. 1-11). Two years later McCollum employed the first copper sulfate electrode, which since then has generally succeeded in measuring potential in buried installations. Between 1910 and 1918, O. Bauer and O. Vogel at the material testing station in Berlin determined the current density required for cathodic protection [42]. In 1920 the Rhineland cable near Hanover was damaged by corrosion as a result of geological factors in the soil, and for the first time in Germany zinc plates were built into the cable shafts to protect the metal sheathing [32]. The protection of iron by electric current was eventually the subject of a dissertation in 1927 [43].

By 1920 welding technology had reached a stage at which safe welds could be reliably produced and as a consequence continuously welded transmission pipelines could be constructed. Thus, there appeared to be nothing to hinder a common application of cathodic protection. Peterson [44] reported an electrical process for protecting pipelines against rust which had also given excellent protection against soil currents in a Galician oilfield. That this report did not lead to the use of cathodic protection was probably the fault of the engineering-oriented builders of pipe networks, who regarded electrochemical protection as a black art. Even electrical engineers overestimated the costs of the process and the danger to other pipelines from the applied currents. Instead, therefore, attempts were made to improve the resistance of pipe coating materials to aggressive soils and to reduce the danger of stray current corrosion by insulating joints.

Cathodic protection of pipelines did not develop in Germany but it was applied from 1928 onward in the United States. Figure 1-12 shows a medal with the head of Robert J. Kuhn, called the "Father of Cathodic Protection" in America. He installed the first cathodic protection rectifier in 1928 on a long-distance gas pipeline in New Orleans, and thus inaugurated the first practical application of cathodic protection of pipelines. As early as 1923, E.R. Shepard in New Orleans had diverted powerful tramline stray currents with an electrical drainage system. The protection range of plain cast pipes with poorly conducting joints did not extend to the end of the pipeline, so Kuhn put additional protective rectifiers in. He found by experiments that a protective potential of –0.85 V against a saturated copper/copper-sulfate electrode provided sufficient protection against any form of corrosion. At the Washington Conference for Corrosion Protection held by the National Bureau of Standards in 1928, Kuhn reported on the significant value of his experiments, on which the entire modern technology of cathodic protection is founded [45]. Considerable doubt existed in the minds of American scientists at that time over the causes of corrosion of buried pipelines. Kuhn's presentation was the only one that dealt with corrosion resulting from galvanic cell formation. It contained the description of a process that prevented corrosion by application of rectified dc, i.e., by cathodic protection. Kuhn wrote: "This method was not applied exclusively to prevent corrosion but to cut out electrolytic corrosion of the pipeline arising from streetcar stray currents by electric drainage." This application had shown that the pipes were not only protected against

Fig. 1-12 Gold medal with picture of Robert J. Kuhn. The medal was established by the Technical Committee of Cathodic Protection and first awarded in 1970 by the DVGW in Würzburg.

stray current electrolysis but also against galvanic cell currents and thus against soil corrosion. The experiment showed that on average 10 to 20 mA m^{-2} protective current density was sufficient to depress the potential of the pipeline to a value where pitting no longer occurred [46].

Some experts still regarded the experiments with skepticism. The American Petroleum Institute in Los Angeles declared in 1935 that galvanic protective currents from zinc anodes could no longer protect pipelines over the increasing distances being used, and that protection against chemical attack, such as by acids, would be definitely impossible. Since pipelines in America were mostly laid without any insulating coverings until well into the present century, the cathodic protection of such pipelines proved comparatively expensive and required considerable protective currents. It is therefore not surprising that even in the early 1930s only about 300 km of pipelines in America were protected by zinc anodes and 120 km by impressed current. Among them were pipelines in Houston, Texas, and Memphis, Tennessee, which had been cathodically protected by Kuhn from 1931 to 1934. In early 1954, I. Denison was awarded the Whitney prize by the National Association of Corrosion Engineers. Kuhn's discovery was given renewed publicity, for in his acceptance speech, Denison explained: "In the first corrosion protection conference in 1929 Kuhn described how the potential of a pipeline was depressed to –0.85 V against a saturated copper/copper sulfate electrode using a D.C. rectifier. I need not remind you that this value is the accepted potential criterion for cathodic protection used worldwide nowadays."

Smith reported in 1940 [47]:

> "Cathodic protection applied in the United States has had mixed success and variable criticism. Failure is partly due to false evaluation of the active region and partly due to insufficient planning and operation of the plant to be protected. It is partly the failure to recognize that the process against corrosion due to high and widely ranging soil currents arising from stray currents from D.C. installations with correspondingly higher potentials to give protection against them, can only be successful if these currents are drained in addition. The cathodic protection process is only relevant for oil, gas, and water pipelines against soil attack in areas where there are no stray currents. Neither soil composition nor climate can impair the action of the protective medium if the anodic current is sufficient to reduce the potential of the pipeline to be protected against that of the soil by about 0.3 V."

The first anode installation for the cathodic protection of gas pipelines in New Orleans consisted of a 5-m-long horizontal cast-iron tube. Later old tramway lines were used. Since in downtown New Orleans there was no suitable place to install impressed current anodes and to avoid detrimental effects on other pipelines, Kuhn recommended the use of deep anodes which were first installed in 1952 at a depth of 90 m.The first deep anodes were installed in Hamburg in Germany in 1962 by F. Wolf [48] (Fig. 1-13).

Publications on the cathodic protection of pipelines became known in Europe at the end of the 1920s. In Belgium the drainage of streetcar stray currents was widely practiced. L. de Brouwer applied protection to gas supply lines in Brussels from 1932 onward and in 1939 the base plates of a gasholder were also protected with impressed current [49]. In Germany the following report was made in 1939 on the cathodic protection of pipelines [50]: "The following precautions against stray currents should first be taken to prevent the leakage of current from the rails into the surrounding earth. On the pipeline it is advisable to provide it with a double sheath and to choose electrically insulating connections to raise the insulation resistance for a distance of about 200 m either side of its crossing of the tracks. A conducting connection between the pipe and the track should only be made with the greatest caution so that the reverse action does not occur." From Soviet publications on cathodic protection, it appears that by about 1939 more than 500 cathodically protected installations existed in the USSR [51], [52]; judging by their numbers, these utilized sacrificial anodes. Cathodic protection of pipelines by sacrificial anodes appeared in Great Britain after 1940 [53]. In Germany in 1949 the water

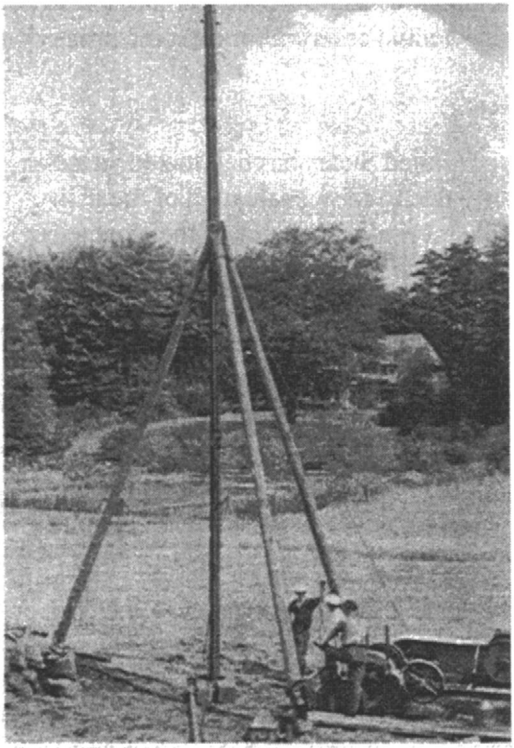

Fig. 1-13 The first deep anode for cathodic protection in Germany.

supply network of the Brunswick brown coal mines were cathodically protected by zinc plates by W. Ufermann [54]. Figure 1-14 shows the cathodic protection installation in the Palatinate near Bogenheim, which was installed together with other protective measures against stray current by Saar-Ferngas in 1952. In 1953 in Duisburg-Hamborn [55] and in 1954 in Hamburg [56] particular cathodic impressed current systems had been installed to protect limited parts of old long-distance gas lines. After 1955 these were extended to all pipelines and in particular newly installed long-distance gas supply lines. However, in spite of the obvious advantages of cathodic protection, even for single-wall storage tanks buried in soil, it was only in 1972 that a directive was enacted [57].

In the past few years the technique has developed from local cathodic protection to the cathodic protection of the underground installations of whole power stations and industrial plants (see Chapter 12). Since 1974 cathodic protection has been compulsory in Germany for gas pipelines with pressures over 4 and 16 bars (DVGW instructions G462 and 463 respectively) and for oil pipelines according to the guidelines for transport of dangerous liquids by long-distance pipelines (TRbF* 301).

The basic standard for cathodic protection was laid down for the first time in DIN 30676 to which all the application areas of the different branches of protection can be referred. In this the most important point is the technique for accurately measuring the object/soil potential [58]. The usual off-potential measurement method for underground installations has been slowly implemented and enforced in Europe since the 1960s [59].

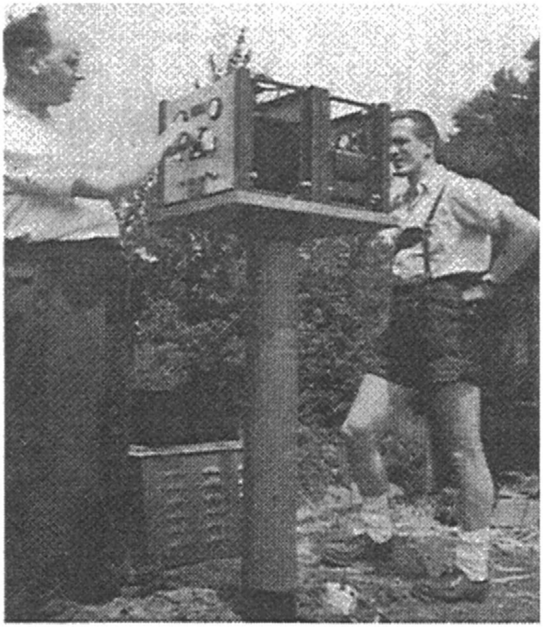

Fig. 1-14 Cathodic protection rectifier manufactured in France (1952) at Bogenheim in the Palatinate.

1.4 Development of Stray Current Protection

The first news of the destructive influence of stray currents reached Europe from America shortly before the turn of the century. Stray current electrolysis as a new corrosion hazard for buried pipes as a result of increasing domestic dc supplies and the construction of direct current railways also became evident in Germany. Werner von Siemens introduced at the 1879 Berlin Gewerbeausstellung (Trade Exhibition) the first direct current electric railway in the world. The first electric tram to Berlin-Lichterfelde ran 2 years later using a positive and a negative rail with an operating voltage of 140 V. In 1882 Siemens installed an experimental tram service with overhead supply, running from Westend to Spandauer Bock. As shown in Fig. 1-15, the line was initially equipped with two overhead wires so that the escape of stray currents into the soil was prevented [60]. Unfortunately, it was not possible to retain this system.

The first underground railway in the world was opened on January 10, 1863 in the City of London, operating with steam locomotives. The first line with electric traction and a three-rail system was built in 1890. The four-rail system, still in use today and consisting of two insulated conductor rails and two running rails, was introduced in 1903 in the course of electrification of the old steam tracks. The Metropolitan Company, responsible for a part of the track, used ac, while the District Railway preferred dc as a consequence of the connection with the American railways. This dispute came before a British arbitration tribunal in 1900. The problem of corrosion of public supply lines by the returning current from electric train

Fig. 1-15 Berlin streetcar in 1882 with double overhead conductor with rod contact.

locomotives was at that time already appreciated as a result of the considerable difficulties encountered in America, and the advantage of the ac system was that these inconveniences were eliminated. The arbitrators solved the problem by recommending the use of 600-V direct current and also the laying of a return-current rail insulated from the running rails [61].

The first serious electrically induced corrosion damage in the field of tram rails appeared in 1887 at Brooklyn on forged iron pipes, and in the summer of 1891 at Boston on the lead sheaths of telephone cables [62]. The first commission to investigate the phenomenon of stray currents was set up in America.[2] The commission recorded that considerable differences in potential exist between pipes and the track of electric railways, and that the pipes are endangered in positions "where the charge is positive and the current escapes into the electrolysis-prone surroundings." It was found experimentally by Flemming that iron surfaces buried in damp sand with a potential of +0.5 V and a current of 0.04 A corroded visibly after only a few days. The first direct stray current drainage was installed in 1895 by E. Thompson for the Brooklyn tramway in an attempt to move the stray current directly back to the rails without harmful effects [63]. However, this occasionally caused such a powerful increase in the stray currents that they melted the lead seals of the joints.

Deliberate stray current drainage was installed at a subrectifier in Germany as early as 1895 during the electrification of the Aachen tramway. The effective protection extended over a relatively small field since the comparatively large resistance of the pipe joints did not permit a greater extension of protection.

The Berlin City electrical engineer M. Kallmann reported in 1899 on a system for controlling stray currents of electric railways [64]. As early as 1894, the Board of Trade in London issued a safety regulation for the British electric railways which specified a potential differential of not more than 1.5 V where the pipeline was positive to the rails, but 4.5 V with the rails positive. Extensive research was undertaken on reducing the risk of stray current in the soil by metallic connections from pipes to rails. However, as one writer noted, "a procedure on these lines should definitely be discouraged as it carries the seed of its own destruction" [64].

The *Journal für Gasbeleuchtung* mentions electrolytic corrosion damage caused by direct current cables in Berlin in 1892, and a few years later damage by tramway currents was reported in 14 German towns. As early as 1894 the electrolytic processes of stray current corrosion were explained in detail in this journal by G.Rasch [65].

In 1910, a joint commission of the associations of German electrotechnicians and gas and waterworks engineers issued regulations for the protection of gas and

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[2] Around 1890 about 100 tram lines were run by direct current in Germany and well over 500 in America. In 1981 there were only 33 such local trams in the Federal Republic and 25 in the German Democratic Republic.

water pipes against the harmful influence of currents from electric dc railways that used rails as conductors. These, however, forbade direct returning of stray currents to the rails. Attempts were made to reduce stray currents by incorporating insulating joints and improving the pipe coverings. This was mainly restricted to points where tram lines were crossed in order to economize on insulating flanges. This often resulted in new escape points for the stray current at the insulating flanges. To avoid the prohibited direct connection with tram rails, in regions of stray current, an exit connection was made to uncoated protective pipes or to iron girders buried alongside the rails. That the problem could not be solved in this manner was very soon recognized. Only in 1954 did a new version of VDE* 0150 establish a legal basis in the Federal Republic of Germany to sanction the stray current conductors and drains installed since 1950 [17]. In 1966 a joint group for corrosion problems, the Arbeitsgemeinschaft für Korrosionsfragen or Working Association for Corrosion Questions (AfK) and the Arbitration Board for Relevant Problems, decided on measures to protect pipelines against increasing high-tension effects by using better coatings [66].

The principles of stray current drainage by rectifier as practiced today depend on impressed current cathodic protection as described by H. Geppert. In his patent Geppert referred to the fact that stray currents escaping from a pipeline will be compensated, and he also mentions the possibility of a direct connection of the protective current source with the rails. A direct connection without additional impressed current between pipeline and rails is sufficient only with permanently negative rails, as for instance near rectifier installations. As early as 1930, 25 direct stray current drainages for post office cables existed in Milan and Turin. It is necessary to install return current blocks in the connections where rails become even temporarily positive. In 1934, L. de Brouwer, the Chief Engineer of Distrigaz, installed one of the first polarized relays in Fontaine-l'Eveane near Brussels [67,68]. By installing rectifiers into a temporary drainage connection in Berlin in 1942, reverse current was prevented. Figure 1-16 shows the first drainage relays made in Germany, which were installed for the protection of a long-distance pipeline near Immigrath in 1953.

A protective rectifier between pipeline and rails that was installed by Kuhn in 1928 was the forerunner of modern forced drainage. This form of controlled stray current drainage was developed further, particularly in France, in combination with stray current relays. The first such polarized drainage was installed at Bad Dürheim in 1975 and had an appearance similar to the cathodic protection rectifier in Bogenheim, shown in Fig. 1-14. Today mainly controlled potential rectifiers are used for stray current drainage. The first of these, in Wuppertal-Cronenberg, conducted peak currents of more than 200 A between 1961 and 1970.

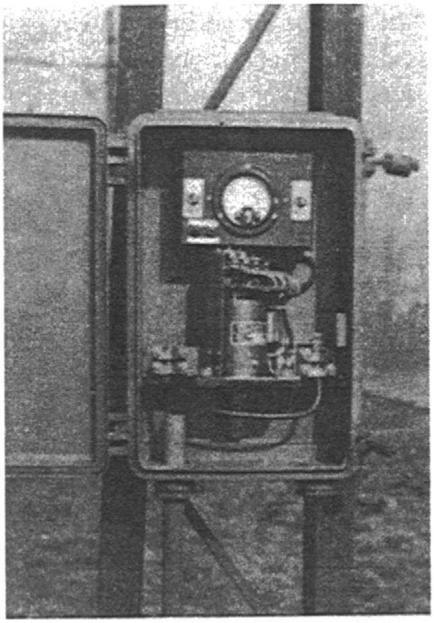

Fig. 1-16 First polarized relay for stray current drainage in Germany at Immigrath in 1953.

1.5 Corrosion Protection by Information

The question of corrosion and corrosion protection has become even more important with the increased use of metallic materials as industry has grown. The concern over the great number of avoidable failures compelled an investigation of the causes for which in most cases organizational problems had been indicated [69]. It also showed that the science of corrosion protection had spread into diverse technical areas almost unsurveyed. The Arbeitsgemeinschaft Korrosion founded in 1931 was reconstituted in 1981 as a registered association with a scientific advisory committee. In the new statute its purpose was designated as the coordination of technical regulations as well as research and the exchange of experience. The information given in this handbook is largely contained in the DIN standards which were formulated and mutually agreed upon by the standard committees NAGas 5.2 and NMP 171. In this respect, the conceptual standards DIN 50900 and the basic standards for electrochemical protection, DIN 30676 and DIN 50927, are particularly relevant.

To provide a better survey, the Arbeitsgemeinschaft Korrosion undertook the sifting of the regulations collected by the Deutsche Informationszentrum für Technik and published them in an industry-related compilation with an advisory commentary [70]. Updates continue to be published in the journal *Werkstoffe und Korrosion.*

The state of the art in 1987 was published in "Survey of standards, technical rules and regulations in the area of corrosion, corrosion testing and corrosion protection," together with the most important DIN standards and some other regulations in the DIN 219 [71]. A commentary on these standards has also appeared [72].

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