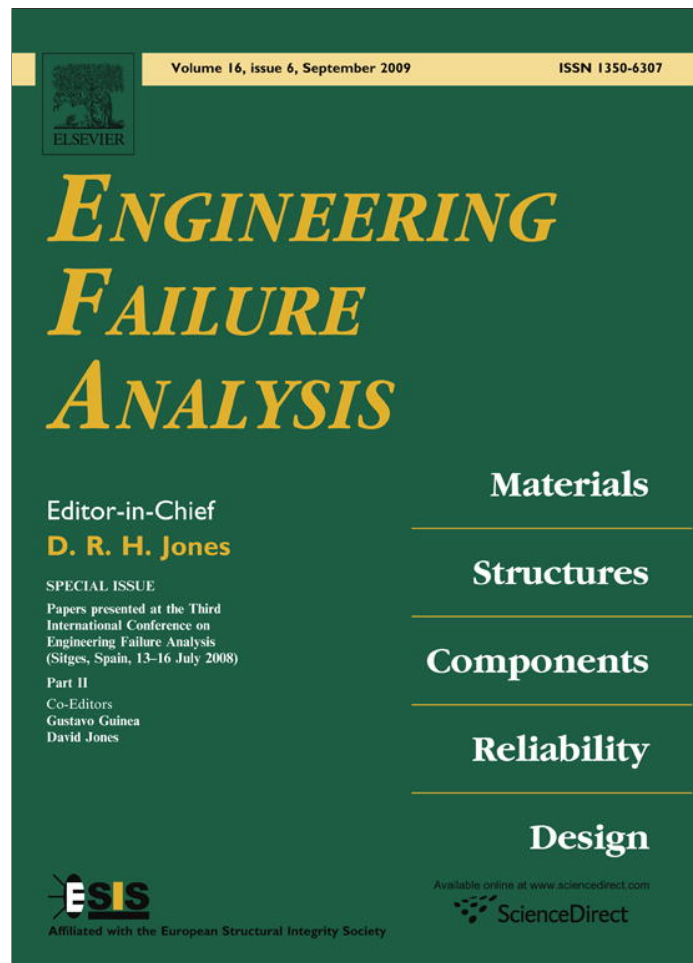


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

Engineering Failure Analysis

journal homepage: www.elsevier.com/locate/engfailanal

Root causes of fire in a solvent pipe at a petrochemical plant

J.L. Otegui^{a,*}, P.G. Fazzini^b^a INTEMA – University Mar del Plata – CONICET, J.B. Justo 4302, (B7608FDQ) Mar del Plata, Argentina^b GIE S.A. Galicia 52, (B7608AUB) Mar del Plata, Argentina

ARTICLE INFO

Article history:

Received 19 September 2008

Accepted 23 September 2008

Available online 2 October 2008

Keywords:

Petrochemical plant

Pipe failure

High temperature

Maintenance

ABSTRACT

The root causes of a leak followed by a small fire in a 2 in. solvent pipe in a Petrochemical Plant are discussed. The fire occurred during blanket heating to 300 °C to dissolve polymer clogs. Fractographic and metallographic analyses showed that the failure is characterized by intergranular through the thickness propagation of longitudinal cracks initiated at the outer pipe surface. This cracking mode is called r-type cavitation. The leaking solvent self ignited, polymer deposits inside the pipe carbonized, microstructure changed. All these indicate that pipe temperature during blanket heating reached 550 °C, much above the specified 300 °C maximum. At this temperature yield strength of the pipe material got below nominal hoop stress due to normal internal pressure. The failure of the temperature control system in one of the heating blanket sets was the main event that caused the fire. However, other conditions and exceeded barriers are discussed, related with safety procedures and insufficient support of the ongoing investigation by the contractor involved in the incident. As a result, changes in the declogging and safety procedures were introduced.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

A small fire occurred near midnight, in a 2 in. diameter, 5.6 mm thick solvent injection pipe, made of ASTM A53 Gr. B steel, during the application of thermal blankets in order to increase the temperature of the tube to 300 °C. This procedure is used to cause the liquefaction of solid polymer residues that clogged the pipe, produced by in-service polymer reflux, and in that way to facilitate their removal. This failure was detected by a security person; its relevance as a possible source of a major fire or explosion accident was immediately acknowledged. First root cause analyses were carried out by the contractor in charge of the declogging operation. Unfortunately, the aim to avoid responsibilities distorted the outcome of the analysis.

Fig. 1 shows the failed section of the pipe, the leak is indicated by a white arrow. The solvent inside the pipe leaked in the heated section and self ignited, creating a fire jet that ended quickly.

The solvent in the pipe is called Isopar-E (produced by Exxon), mixed with ethylene, with dissolved octene (or butene) and hydrogen. Normal operation temperature is 40 °C, working pressure varies between 50 and 65 bar. Under those conditions the mixture is in liquid phase. In certain occasions, the reactor is taken out of service and the solvent injectors are washed. This is a routine procedure carried out at least monthly. In this case the feed is only Isopar at a temperature in the range 180–230 °C, for a period of 4–10 h (depending on how dirty the injectors are found).

This solvent remains liquid at the nominal service pressure of 5 MPa up to around 320 °C. Manufacturer data [1] indicates that the temperature of self ignition (that is, ignition without flame) is 380 °C. Other data of the Isopar are [2]:

* Corresponding author.

E-mail address: jotegui@fi.mdp.edu.ar (J.L. Otegui).

URL: <http://www.giemp.com.ar> (P.G. Fazzini).



Fig. 1. Failed section of the pipe.

- Critical temperature: 320 °C.
- Critical pressure: 18.5 atm.
- Density of liquid (among 25–100 °C): $\text{dens} = 735.18 - 0.8899 * \text{Temp}$.
- Self ignition temperature: 382 °C.
- Thermal conductivity: 0.00028 cal/(s cm °C).

Temperature of carbonization of the polyethylene (PE) is 500–550 °C (in nitrogen atmosphere) [3]. Although blankets have been placed in pipes in several opportunities (two or three times a year), this technique was never used in the failed pipe before.

2. Initial hypothesis

An essential aspect in this case is to determine the influence of possible deviations in the parameters of heating time and temperature in the occurrence of the accident. Possible sources of methodological error were evaluated, such as eventual flaws in thermocouples and control devices. Unfortunately, blankets and control units were removed from premises before this study began. Moreover, the first explanation assessed was that the procedure was intrinsically unsafe: if for some reason the clogs completely stopped the flow inside the pipe, then the trapped liquid would vaporize under the action of the blanket heating, leading to high pressure and eventual failure by yielding of the pipe.

Visual evidence seemed to validate this initial hypothesis. Fig. 2 shows the failed section, after cleaning. A ½ in. long longitudinal crack is very open, this is the origin of the leak that produced the fire. The figure also shows a colony of many other although smaller longitudinal cracks. Noticeable in Fig. 1 is also the large increase in diameter in the affected region. Diam-



Fig. 2. Failed section of the pipe after cleaning.

Table 1

Calculations of the pressure increase by the thermal expansion of Isopar-E.

Thermal expansion coefficient of Isopar-E @ 150 °C (average temp.) = $1.758\text{E}-3 \text{ } ^\circ\text{C}^{-1}$	$V_f = V_o * [1 + C_t * (t_f - t_o)] = 10 \text{ l} * [1 + 1.758\text{E}-3 * (300 - 20 \text{ } ^\circ\text{C})] = 14.9224 \text{ l}$
Metal expansion of pipe (considering iron cubic expansion coefficient)	$V_2 = V_1 * [1 + C * \Delta T] = 10 \text{ l} * [1 + 0.355\text{E}-4 * 280 \text{ } ^\circ\text{C}] = 10.1 \text{ l}$
Compressibility coefficient of Isopar-E @ 100 °C (best value found) = $5.8\text{E}-4 \text{ atm}^{-1}$	$V_f = V_o * [1 - C_p * (P_f - P_o)] \Rightarrow P_f = [1 - (V_f/V_o)]/C_p + P_o = [1 - (10.1/14.9224)]/5.8\text{E}-4 + 59 \text{ atm} = 557 + 59 = 616 \text{ atm} = 624 \text{ barg}$

eter mapping showed maximum increase in diameter of (around 20%) over a length of around 5 in., where all cracks are located. The rest of the pipe does not show apparent distortions.

The failure mode was by longitudinal cracks developed from the outer surface of the pipe wall. These cracks are driven by maximum hoop stresses, which are due to inner pressure. Operator data allows considering an inner nominal pressure of around 6.5 MPa. For a 50 mm diameter, 5.6 mm thick pipe, Barlow equation defines a nominal hoop stress of 29 MPa. This is 12% of the SMYS for the material at room temperature, and around 25% of the allowable stress according to ASME BPVC code [4].

When heating, it is possible that solvent got trapped between two consecutive clogs. Table 1 includes the initial calculations of the pressure increase by the thermal expansion of the Isopar-E. It considered a 5 m long pipe totally full with Isopar and covered in both ends, heated up to 300 °C. A pressure increase of as much as an order of magnitude was calculated. Considering a perfectly tight pressure chamber, perfectly filled with liquid solvent subjected to a temperature increase of around 300 °C means that inner pressure multiplies by 20. Therefore, in this event a maximum inner pressure of twice the material SMYS could have been reached at 300 °C.

This preliminary conclusion, although satisfactory for the contractor, meant that a normal maintenance procedure for the company proved unsafe, and had to be modified. Therefore, a thorough root cause analysis was assigned to a third party specialized in failure analysis [5].

3. Visual and metallographical analysis

Cross-sections were cut at different locations, including the failure place, and samples identified. The inside of the pipe revealed diverse degrees of clogging, depending on the section. Fig. 3 shows that at the failed section the polymer clog is carbonized, while at other sections the clog remains white, see for example Fig. 4. The carbonized PE region spans a 500 mm length of pipe. The clog is layered, revealing different stages of deposition. The clog revealed soft and porous. Pneumatic tests revealed that most sections do allow the passage of low pressure air. There is also evidence of solvent flow during the heating process.

Table 2 shows the results of a diameter and thickness mapping around and far from the failed section. Maximum thickness reduction is more than 40%, and occurs in the failed section. Largest plastic deformations in the pipe material occur in the areas of the perimeter where polymer residue is thicker. This occurs in the failed region (Fig. 3) but also in other sections affected by the heating. Fig. 5 shows sections where polymer residue is thinner.

Possible microstructural variations in the failed section, and the size, morphology and orientation of cracks and defects in that region were assessed. Circumferential specimens from each section were polished and Nital etched, as shown in Fig. 6 ($\times 3$). In these and the following pictures, outer diameter is placed at the top.



Fig. 3. Carbonized polymer clog in the failed section.



Fig. 4. Not carbonized polymer clog away from the failed section.

Table 2
Diameter and thickness mapping around and far from the failed section.

Distance (mm)	Diameter (mm)	Thickness range (mm)
20	67	Minimum: 3.93, maximum: 5.00
40	67.2	
60	66.7	
80	66.7	
90	66	
100	67.7	
120	69	Minimum: 3.3, maximum: 4.94
140	70	
160 LEAK	71.3	
180	70.8	
200	70.8	Minimum: 4.13, maximum: 4.67
220	70	
240	69	Minimum: 5.35, maximum: 5.45
260	68.6	
280	68.8	
300	69	
320	68.5	
340	62.2	
360	63.5	
380	65	
400	65.9	
420	66.8	
440 → 800	60.8	5.6



Fig. 5. Sections where polymer residue is thinner.



Fig. 6. Polished and Nital etched circumferential specimen.

Fig. 7 ($\times 50$) shows the microstructure near the failed section, close to the outer pipe surface. The lighter colour of a 0.2 mm thick subsurface layer indicates severe decarburization; and many branched through the thickness cracks initiate from the outer surface. Fig. 8 ($\times 50$) shows the microstructure near the failed section, close to the inner pipe surface. The darker colour of a 0.35 mm thick subsurface layer indicates severe carburization.

Decarburization is evident near both surfaces in non damaged sections, but is always more severe at the outer surface. Pearlite grains within a ferritic matrix are typical for this type of steel. Also typical is the longitudinal microstructural banding, produced during forming of the pipe.

Fig. 9 ($\times 200$) shows the thickness crack that led to gas leakage and fire. Near the inner pipe surface, grains are elongated, indicative of large plastic deformations, while near the outer surface crack path is intergranular. Fig. 10 ($\times 200$) shows details of the other side of this crack, near the outer pipe surface. Note the intergranular path, many small secondary embedded intergranular cracks are seen at both sides of the main crack.

More detail of the intergranular nature of the main crack and the secondary cracks in the mid thickness of the pipe wall is seen in Fig. 11 ($\times 500$). Note the mostly ferritic microstructure, which is representative of most of the thickness. This contrasts with the acicular microstructure in the carburized layer close to the inner wall (Fig. 9).

It is concluded that the leak was produced by the intergranular propagation of a crack initiated at the outer, decarburized surface of the pipe. This was only one of the many intergranular cracks initiated in that surface, other similar cracks in different stages of development are seen for instance in Figs. 3 and 7. These secondary cracks have depths ranging from 0.1 to 0.5 mm, but most of them span the decarburized surface layer.

The pipe steel is an ASTM A53, low carbon, low strength C–Si–Mn ferritic pearlitic steel. Main chemical elements are C 0.17%, Si 0.22%, Mn 0.63%, S and P are low, around 0.01%, all these are within specifications. Its strength and toughness do not strongly depend on thermal treatment. This steel has room temperature yield strength of 240 MPa, and an ultimate stress of 415 MPa. As Table 3 shows, yield strength drops drastically with temperature increase [6]. Strength remains almost constant until 300 °C, drops to half at around 400 °C, while at 500 °C strength is only 10% of the strength at room temperature. Average hardness is 170 HV in the failed region and 155 in sections far from the leak, with little variation through the thickness.



Fig. 7. ($\times 50$) Microstructure near the failed section, outer pipe surface of pipe wall.



Fig. 8. ($\times 50$) Microstructure near the failed section, inner pipe surface of pipe wall.



Fig. 9. ($\times 200$) Crack that led to gas leakage and fire.

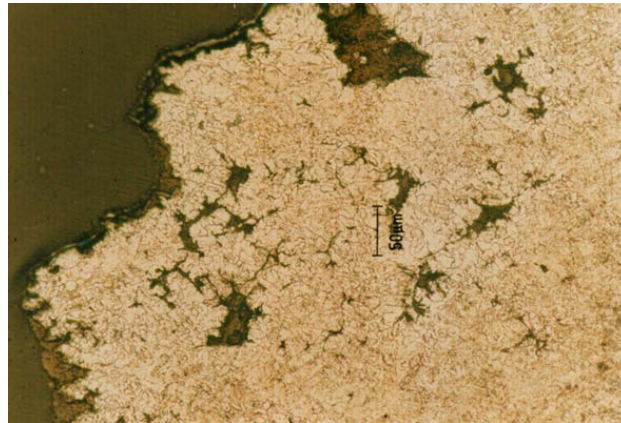


Fig. 10. ($\times 200$) Secondary cracks, wide open, near outer pipe surface.

4. Conditions that lead to failure

The failure mode was by longitudinal cracks developed from the outer surface of the pipe wall. These cracks are driven by maximum hoop stresses, which are due to inner pressure. Original calculations by plant owner showed it was possible that a temperature increase of 300 °C could have multiplied internal pressure by 20, if the solvent was perfectly trapped within the pipe, so that hoop stress can easily reach material yield strength. This was a simple, attractive and wrong explanation, that could have led to costly changes of operation practices throughout the company [7,8].

Experimental evidence shows that most of the pipe was filled with PE residue, a soft, sponge-like elastic material. There is also evidence of flow inside the pipe during heating. An eventual unexpected increase in temperature above the specified

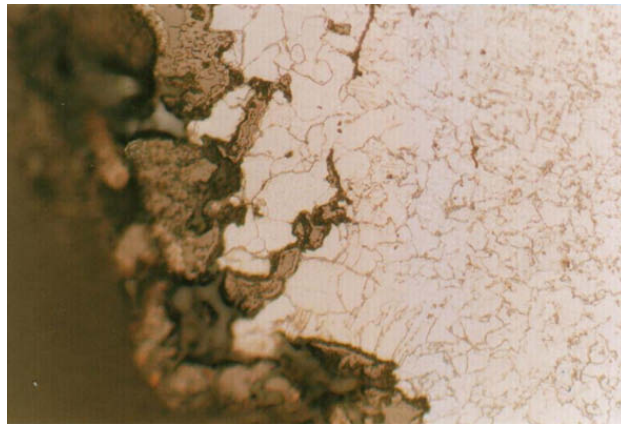


Fig. 11. ($\times 500$) Detail of intergranular nature of the main crack.

Table 3

Evolution of yield strength with the temperature.

Temperature ($^{\circ}\text{C}$)	Yield strength (Mpa)	Allowable stress (Mpa)
0	241	117
50	241	117
100	215	117
150	198	117
200	182	117
250	165	117
300	149	117
350	136	110
400	128	89
450	–	59
500	–	32
550	–	15

300 $^{\circ}\text{C}$ deeply decreases material strength (Table 3), above 530 $^{\circ}\text{C}$ failure occurs at normal pressure, it is therefore possible for failure to occur in the absence of pressure increases. Therefore, evidence of such a temperature increase was searched for.

Heating of the pipe was achieved by means of blankets placed in tandems of three, each tandem is controlled individually. Temperature is controlled by one thermocouple in one of the blankets of each tandem, outputs of every three thermocouples are plotted together. Fig. 12 shows the temperature evolution indicated by three thermocouples, the readings of the thermocouple involved in the failed section is indicated by an arrow. Note that scatter is very low in the one channels, while dots are somehow more scattered in the other two channels. After a stepped temperature increment, at 10:00 AM the specified maximum temperature of 300 $^{\circ}\text{C}$ was reached. Fig. 12 shows that the thermocouple at the failed tract starts an erratic behaviour shortly after 10:00, and at around 11:20 dots disappeared. Heating, however, continued.

At the moment of the break the section withstood 14 h of heating, but maximum temperature at the failed section is uncertain. Plant information is that these blankets are designed for standard heat treatments, and can reach temperatures near 1000 $^{\circ}\text{C}$.

It is clear that it cannot be ensured that the failed section was kept at the specified maximum temperature of 300 $^{\circ}\text{C}$.

Metals undergo a transition from transgranular fracture to intergranular fracture as the temperature is increased. When transgranular fracture occurs, the slip planes are weaker than the grain boundaries, while for intergranular fracture the grain boundary is the weaker component. The equi-cohesive temperature (ECT) is the temperature at which the grains and grain boundaries have equal strength. Like the recrystallization temperature, the ECT is affected by stress and strain rate. Decreasing the strain rate lowers the ECT and therefore increases the tendency for intergranular fracture. The effect of strain rate on the strength–temperature relationship is believed to be much larger for the grain-boundary strength than for the strength of the grains. Since the amount of grain-boundary area decreases with increasing grain size, a material with a large grain size will have higher strength above the ECT than a fine-grain material. Below the ECT the reverse is true [9].

Ordinary ductile fracture, initiated at inclusions and second-phase particles, can extend to rather high temperatures. At the lower flow stresses existing under power-law creep the same type of ductile fracture mechanism exists. However, since the metal is creeping, the stresses within it tend to be lower than for ductile fracture and the nucleation of voids is postponed to larger strains. Also, because of the strain-rate dependence of creep, the flow can be stabilized and void coalescence be postponed. Fracture in this case is transgranular. At lower stresses a transition from transgranular to intergranular fracture occurs. Within this region grain-boundary sliding becomes prevalent and wedge cracks and voids grow on the grain boundaries in a direction normal to the tensile axis. At the highest temperature, if no other fracture mechanism intervenes, the

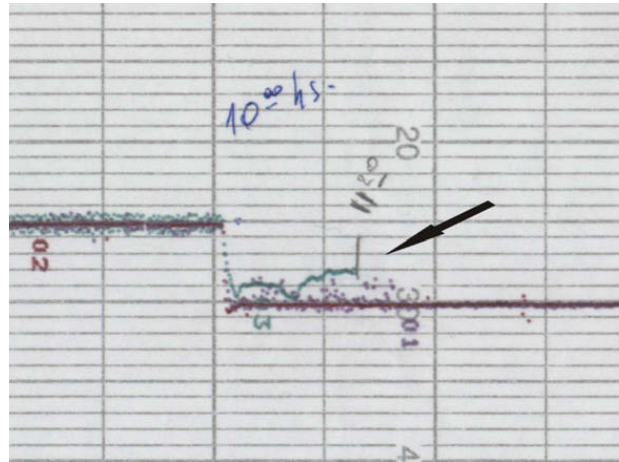


Fig. 12. ($\times 200$) Temperature evolution during blanket heating.

material becomes mechanically unstable and necks down to a point. This requires that the nucleation of voids be suppressed or that coalescence of voids not occur. This type of ductile rupture behaviour is observed when dynamic recrystallization prevents void linkup and coalescence.

It is well documented that cavities form continuously throughout the creep process. However, in the third stage of creep the nucleation and growth of grain-boundary voids and cracks occurs at an accelerated rate. This process is frequently called creep cavitation. Analysis of the problem indicates that extremely high stresses normal to a grain boundary are required to nucleate a cavity. Thus, very large stress concentrations are required. These large stress concentrations can be produced at particles in sliding grain boundaries, at the intersection of slip bands and grain-boundary particles, and at grain-boundary triple points. However, under creep conditions the generation of high stress concentrations is moderated by both power-law creep and diffusional creep processes. This explains why numerous cavities are not formed at the beginning of a creep process, but rather they accumulate with time. The nucleated cavity must be large enough to grow in the face of capillarity forces which tend to make it shrink.

Two types of intergranular cracks occur in creep [9]. Wedge-shaped cracks (w-type cracking) initiate mostly at grain boundaries which are aligned for maximum shear. They initiate by grain-boundary sliding. Round or elliptical cavities (r-type cracks) form in the grain boundaries that are aligned normal to the tensile stress. This is clearly the case under study, see for example Fig. 13 ($\times 200$, applied tensile hoop stress is horizontal). Extensive studies of this growth mechanism show that cracks grow by diffusion when they are small, but as they become larger power-law creep becomes the dominant growth mechanism. As the strain rate is decreased or the temperature is raised the r-type cavitation is favoured over the w-type.

There is a bound on strain rate above which wedge cracking is not possible. If the elongation or reduction of area is measured with increasing temperature from room temperature, there is usually an intermediate temperature region of low ductility. This region of minimum ductility typically occurs just below the recrystallization temperature, in a region where grain-boundary sliding can occur to produce intergranular cracking. When the temperature is raised beyond the ductility minimum into a region where recrystallization can occur readily, these new grains isolate the grain-boundary cracks and the ductility is increased.

5. Discussion of results and conclusions

The failure under study occurred due to an excessively high temperature, which put the material into a very brittle condition at a temperature below recrystallization. The material strength dropped dramatically, and the failure mode became intergranular crack propagation, in a mode called r-type cavitation. The excessive temperature is most probably the result of the failure of the temperature control system of the blanket sets.

Experimental evidence indicates that maximum pipe temperature during blanket heating reached more than 500 °C:

- The leaking solvent got fire with no evidence of an external flame at the moment of the failure, so it can be concluded that the failure occurred at a temperature above the temperature of self ignition for the solvent. This is above 380 °C.
- Table 1 shows that yield strength of the pipe material gets below nominal hoop stress at around 530 C.
- Microstructural analysis reveals a r-type intergranular crack propagation, typical at a temperature a little below recrystallization temperature.
- Polymer deposits inside the pipe are carbonized in a 500 mm pipe length around the leak section, in an inert atmosphere PE carbonizes at around 550 °C. This temperature was not due to the fire forthcoming fire after the leak, since the isolating blankets were held in place during the fire.

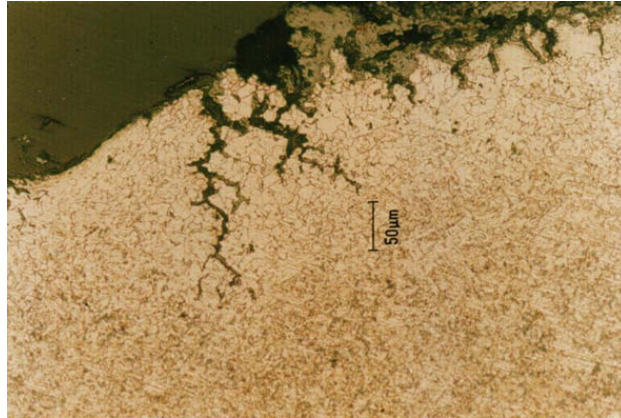


Fig. 13. Case under study, r-type cracks aligned normal to the tensile stress.

- Maximum plastic deformations in pipe material occur in the areas of the perimeter where polymer residue is thicker. Higher heat dissipation by the solvent flow through the channels within the clog kept adjacent pipe material at a lower temperature, thus reducing loss of strength.

There are also other indications of extended exposure to very high temperatures in the failed section of the solvent pipe, all related to accelerated diffusion mechanisms that modified the original ferritic pearlitic microstructure of the pipe steel:

- decarburization near the outer wall surface,
- carburization near the inner wall surface,
- destruction of the lamellar pearlite throughout the pipe wall thickness.

According to operations information, possible previous creep damage due to repeated heating of the affected section can be ruled out, since no previous heating was carried out on this pipe.

Root causes of the failure are of two types:

- Event: the excessive temperature is most probably the result of the failure of the temperature control system of the blanket sets.
- Exceeded barrier: several errors in control during a critical procedure of in-service heating process in the petrochemical plant.

Although this was only an incident, it is clear that an open fire is a very serious condition in a petrochemical plant, which could have had more serious consequences. There were other nonconformities, of which one of the most important is the reluctance of the contractor that generated the unsafe situation to make all pertaining information available to the investigating team. It is now understood that the contractor most probably immediately knew the nature of the problem. By attempting to hide the evidence, the contractor would have lead the operator to carry out major modifications in the procedures for cleaning clogs, with the added costs and possible new risks that this could have added to the operation of the plant.

Acknowledgements

This research work was funded by CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina) and Dow Chemical Co. Thanks are given to Dow Argentina and GIE S.A. (Plant Integrity Division, Argentina) for technical and financial support and for permitting publication of proprietary information.

References

- [1] Isopar-E safety sheet. USA: Exxon; 1999.
- [2] ExxonMobil Chemical. Data sheet; 2007.
- [3] Takuma K, Uemichi Y, Ayame A. Product distribution from catalytic degradation of polyethylene over H-gallosilicate. Amsterdam: Elsevier; 1991.
- [4] ASME Boiler and Pressure Vessel Code. American Society of Mechanical Engineers; 1999.
- [5] Report GIE 2401-09-04. Failure analysis of solvent pipe. EPE plant, PBB Polisor; 2004.
- [6] ASTM A106. API 5L and ASTM A53 seamless carbon steel pipes – pressure and temperature ratings; 2007.
- [7] Kletz Trevor A. Learning from accidents. 2nd ed. Butterworth–Heinemann; 1994.
- [8] Lee Hung Kwong. Safety management. The Hong Kong experience. Lorrainelo concept design Hong Kong; 1991.
- [9] Baik S, Raj R. Mechanisms of creep–fatigue interaction. Boston: Springer; 1982.