Bacterial leaching kinetics for copper dissolution from a low-grade Indian chalcopyrite ore

Cinética de lixiviação por bactéria para a dissolução de cobre de um minério de calcopirita de baixo teor encontrado na Índia

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Resumo

Biolixiviação de cobre (0,3%) de um minério de calcopirita de baixo teor, extraído em minas de Malanjkhand, usando um isolador mesofílico nativo, predominante *Acidithiobacillus ferrooxidans (A.ferrooxidans)*, é apresentada. Uma biorrecuperação de 72% Cu foi registrada na presença dessa cultura (não adaptada), que aumentou para 75% com a cultura do minério adaptado e cultivado por 35 dias ao 35ºC e pH 2,0, com <50µm partículas. Os dados cinemáticos mostraram mais adequados para o modelo básico de encolhimento controlado por difusão, exibindo lotes lineares de [1- 2/3X- $(1\text{-}X)^{2/3}$] vs temp (X - fração lixiviada). Parece que o papel da bactéria, no processo, é o de converter o íon ferroso para o estado férrico, que oxida a calcopirita para poder dissolver o cobre, mantendo o alto potencial redoxante. O valor da energia de ativação (E_a) foi calculado em 9,6 e 10,8 kJ/mol, para as culturas sem e com adaptação, respectivamente, com temperaturas entre 25-35ºC. Esse mecanismo de lixiviação foi corroborado por identificação fásica XRD e em estudos da resídua da lixiviação.

Palavras-chave: Calcopirita, biolixiviação, *A.ferrooxidans, adaptação, difusão, controle cinético.*

Abstract

Bio-leaching of copper (0.3%) from a low grade Indian chalcopyrite ore of Malanjkhand copper mines, using a native mesophilic isolate predominantly Acidithiobacillus ferrooxidans (A.ferrooxidans), is reported. A bio-recovery of 72% Cu was recorded in the presence of this culture (not adapted), which increased to 75% with an ore adapted culture after 35 days at 35ºC and pH 2.0 with <50µm particles. The kinetic data showed best fit for the diffusion-controlled shrinking core model, exhibiting linear plots for [1- 2/3X- $(1\text{-}X)^{2/3}$] vs time (X-fraction leached). Apparently, the role of the bacteria is to convert the ferrous ion to the ferric state, which oxidizes the chalcopyrite in order to dissolve copper, while maintaining a high redox potential. The activation energy value (E_a) was calculated to be 9.6 and 10.8 kJ/mol for the un-adapted culture and the ore adapted culture respectively in the temperature range 25-35ºC. This leaching mechanism was corroborated by XRD phase identification and SEM studies of the leach residue.

***Keywords**: Chalcopyrite, bioleaching, A.ferrooxidans, adaptation, diffusion controlled kinetics.*

1. Introduction

The bioleaching of copper from sulfide ores and waste in dumps and heaps has been practiced for quite some time (Torma, 1977) and so it is the pretreatment of refractory arsenical gold ores, although the concentrates are treated in bioreactors since 1984 (Watling, 2006; Natarajan, 1998). To engineer these processes, the use of the mechanistic model rather than the empirical logistic equation describing the kinetics is preferred (Dutrizac,1969; Dreisinger,2006). For the kinetics of sulfide mineral bioleaching, the two sub-processes are linked at a pseudo steady state by equating the rate of ferrous iron production from the chemical ferric leach reaction to the rate of consumption of Fe(II) by bacteria. For this, expressions of the two sub-processes are written for production and utilization in terms of the rate of Fe(II) produced per unit surface area of the ore. As sulfur- and iron-oxidizing microorganisms enhance the leaching of sulfide minerals, attempts were made to find kinetic equations capable of representing the biological oxidation of Fe(II) and elemental sulfur by mesophiles (Karimi et al.,2011). In light of an indirect leaching mechanism for sulfides with minimum enzymatic attack, a combination of these kinetic equations with fluid-particle reaction kinetics, such as the shrinking core model, has been widely accepted (Valencia and Acevedo, 2009).

The bio-oxidation of chalcopyrite may be represented as given below:

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^o \tag{1}$$

$$CuFeS_2 + O_2 + 4H^+ \rightarrow Cu^{2+} + Fe^{2+} + 2S^o + 2H_2O \tag{2}$$

Although, the rate of Fe(II) oxidation by oxygen (Eq. (3) without iron-oxidizing microbes at pH 1.5 or higher is extremely low, at 65–80°C and pH1.0, it is comparable to those of bioleaching (Shrihari et al., 1990). At pH 1.5–2.5, at which microbes are active, the oxidation of Fe(II) to Fe(III) [Eq. (3)] can be attributed to the activity of microbes and pH, the latter being controlled by the bio-oxidation of sulfur [Eq. (4)]. Additional elemental sulfur can serve to prevent the precipitation of the Fe(III) formed (Shrihari et al., 1990;Yang et al., 2011).

$$4Fe^{2+} + O_2 + 2H^+ \xrightarrow{\text{Biological}} 4Fe^{3+} + 2H_2O \tag{3}$$

$$S^o + O_2 + H_2O \xrightarrow{\text{Biological}} 2H^+ + SO_4^{2-} \tag{4}$$

The precipitation of iron as jarosite is a problem as it covers the mineral surface (Stott et al., 2000), thus reducing the amounts of Fe(III) in solution and lowering the redox potential leading to decrease copper dissolution (Third et al., 2002).

Malanjkhand Copper Project, India contains copper (0.3%) as chalcopyrite mineral embedded in quartz-pyrite veins. Bioleaching of copper from this ore was recently investigated (Pal et al., 2005). In this paper, the kinetics and mechanism of copper bio-leaching from the low grade ore by *A. ferrooxidans* is reported.

2. Materials and methods

Lean grade copper ore (containing 0.3% Cu) was collected in the form of lumps from the Malanjkhand copper mine (located in Balaghat, Madhya Pradesh, India). The ore was crushed, ground and passed through a 150μm sieve. Representative samples were prepared and analyzed (Table-1) as reported earlier (Pal et al., 2005).

The ore was a granitic rock with disseminated sulfides with chalcopyrite as irregular grains in the veins of quartz. Also, the presence of pyrite and chalcopyrite was noticed as fillings along the fractured zone within feldspar. Quartz was very high (38%) in the ore. XRD identification showed major phases as chalcopyrite ($CuFeS_2$), pyrite (FeS_2) and quartz (SiO_2) whereas bornite was the minor phase.

The micro-organism culture used in this study was a predominant microbial isolate of *Acidithiobacillus ferrooxidans (A.ferrooxidans)*, derived by successive enrichment of a mine water sample in 9K media. The culture thus derived was used in subsequent bioleaching experiments. Separate series of experiments were carried out using un-adapted and adapted cultures. The mesophilic isolate predominantly of *A.ferrooxidans* was adapted on ore at 5% (w/v) pulp density, pH 2.0 and 25°C, and the fully grown active culture was used in leaching. Cell count was done using a Petroff Hauser's Counting Chamber using a biological microscope. Unless specified otherwise, bioleaching was carried out in 500 ml conical flasks with 200 ml of total solution, inoculated with 10% (v/v) liquid culture at 25±2°C and pH 2.0 in an incubator shaker with orbital motion at 120 rev min^{-1}. All the inoculated sets had their corresponding

Particle size (μm)	Fraction retained, %	Cumulative Fraction retained, %	Composition (%)		
			Cu	Ni	Fe
>150	26.87	26.87	0.17	0.14	4.41
150-75	23.13	50.00	0.27	0.22	4.47
75-50	13.63	63.63	0.29	0.12	3.34
<50	36.37	100.00	0.32	0.12	6.62

Table 1
Chemical analysis of different sieve fractions of copper ore.

sterile /control sets prepared under the same conditions with mercuric chloride (0.02 g/L) as bactericide. During experiments, 0.5 mL supernatant samples were mostly taken at 5 days intervals for chemical analysis and pH of the leach solution was maintained on alternate days. Cu, Ni and Fe were analyzed by AAS (Model: GBC-980BT). The iron (II) concentration was determined by titrating against 0.05N potassium dichromate solution. Upon termination of the leaching experiments, the solid residues were dried and samples were taken for chemical analysis and XRD phase identification.

3. Results & discussion

Bioleaching experiments using unadapted and adapted culture predominant with *A.ferrooxidans*

Bioleaching of copper was carried out using bacterial culture predominantly *A.ferrooxidans* as un-adapted and adapted cells in the pH range 1.5-2.5 with mixed particles of <150 µm and 25°C temperature. The bio-recovery was found maximum (41%) in 35 days at pH 1.7 and 2.0 with the adapted culture. Acid consumption was slightly more at 1.7 pH (1.8 mL 10N H_2SO_4) as compared to that of 2.0 pH (0.5 mL 10N H_2SO_4). At the lower pH of 1.5 only 36% Cu recovery was observed with the adapted bacteria. High recovery at pH 2.0 was mainly governed by increasing the bacterial oxidation, which was demonstrated by a high Fe(III) level (0.26 g/L) as compared to that of 1.5 pH (0.10 g/L). The metal recovery above pH 2.0 was low due to the jarosite formation on the ore surface (Stott et al. 2000).

The effect of particle size on copper bio-leaching was investigated (Figure 1). Maximum copper recovery (47.5%) was obtained with <50 µm size material using adapted *A.ferrooxidans* which was higher than that of non-adapted bacteria (40%) and 25°C temperature due to the high metal ion tolerance of the adapted strains. Copper bio-recovery was found to be 29.68% and 38.31% with 150-76 µm and 76-50 µm size particles respectively in 35 days. Recovery of copper was better (32%) in 35 days with <50 µm size ore in control experiment, showing that the ore was partially oxidized. Maximum rise in E_{SCE} of 654 mV was noticed for the bioleaching with adapted *A.ferrooxidans* in 35 days with <50 µm size particles because of favoured biochemical oxidation reaction the bacterial attack on the pyrite and biochemical conversion of ferrous to ferric, thus enabling copper dissolution (Third et al., 2002).

Recovery of copper at different pulp densities at 25°C, 2.0 pH with <50 µm size particles in 35 days is shown in Figure 2. The maximum copper recovery was found to be 47.5% and 44% with the adapted and un-adapted (Bevilaqua et al., 2002) predominant strain of *A.ferrooxidans* as mentioned earlier at 5% pulp density, whereas 32% Cu was leached out in sterile/control experiments. Bio-leaching decreased at higher pulp densities, as 38.5%, 33.04% and 31.19%Cu was dissolved with the adapted culture at 10, 15 and 20% pulp density respectively. At 5% (w/v) pulp density, maximum redox potential of the solutions in 35 days was found to be 390 mV for the control leaching, and 652 and 654 mV with the non-adapted and adapted culture respectively, indicating strong oxidizing conditions and consequently higher metal dissolution (Third et al., 2002; Xia et al., 2008).

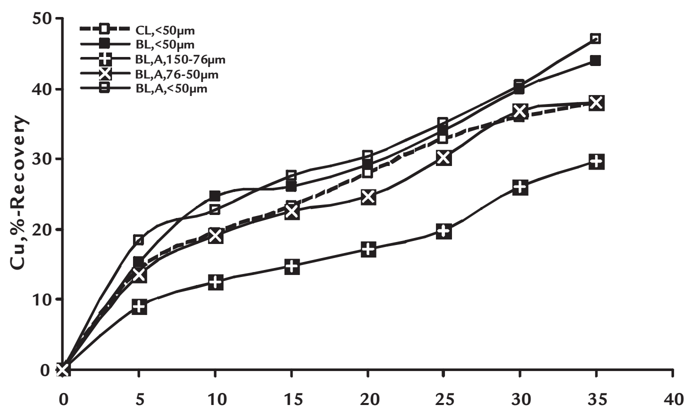

Figure 1
Cu recovery during bioleaching with un-adapted and adapted culture predominant with *A.ferrooxidans* at different particle sizes of ore [pH:2, Pulp Density: 5% (w/v) and Temp: 25°C, BL-A: Bioleaching with adapted culture, BL: Bioleaching without adapted culture; CL: Chemical /control leaching].

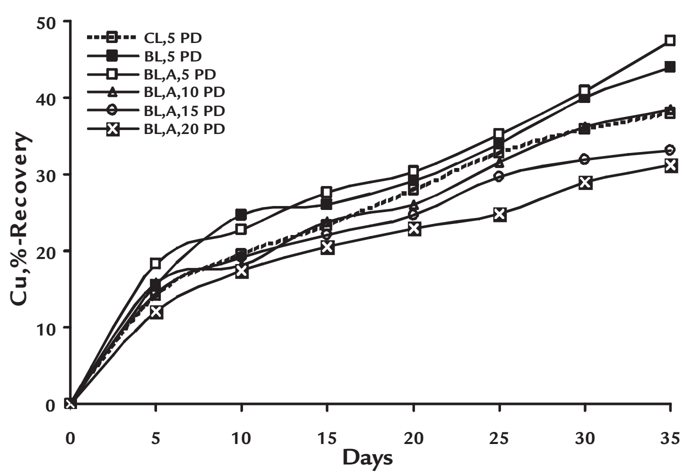

Figure 2
Effect of pulp density on bioleaching of copper with control leaching (CL); unadapted (BL) and adapted (BL-A) predominant culture of *A.ferrooxidans* [Temp: 25°C, Particles: <50 µm, pH: 2].

Effect of temperature on bio-dissolution of copper was investigated in the range 25-35°C at 5% (w/v) pulp density and pH 2.0 and the results are reported in Figure 3. Copper bio-leaching was maximum (75.3%) with the adapted culture (Figure 3b) as compared to 72% leaching with the non-adapted ones (Figure 3a). It is the tolerance limit of the bacterial culture which is enhanced through adaptation leading to the increased metal dissolution (Pal et al., 2005; Xia et al., 2008). Bio-recovery of copper increased from 47.5-75.3% with increase in temperature from 25°C to 35°C. At 35°C, the redox potential varied between 316 to 661 mV and 318 to 668 mV in bio-leaching experiments respectively with un-adapted and adapted cultures, whereas it varied between 312 to 401 mV in control/chemical leaching in 35 days. During bioleaching, increase in bacterial growth was observed from 6×10^7 to 9.8×10^8 and 9.6×10^7 to 11.3×10^8 cells/mL with unadapted and adapted cultures respectively. The higher cell population and redox potential (668 mV) with the adapted cells resulted in higher metal bio-dissolution (Rodriquez et al., 2003). Galvanic interactions does play a role in this case, as the solution with the ore showed an initial redox potential (E_{SCE}) of 303mV; but on addition of culture of un-adapted (Bevilaqua et al., 2002, Qiu et al., 2005; Zhang et al., 2008) and adapted bacteria (Xia et al., 2008), a significant rise in redox potential was noted to respective values of 377 and 403 mV.

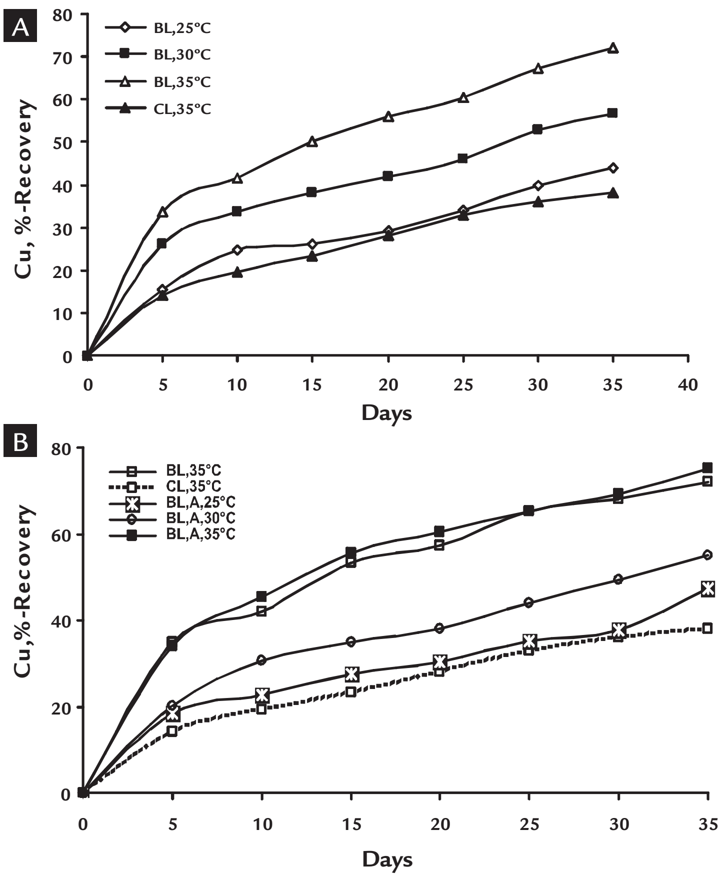

Figure 3
Effect of temperature on copper bio-recovery with culture of (A) un-adapted and (B) adapted bacteria [Particles: <50μm, 2.0 pH, Pulp density: 5% (w/v)].

Kinetics of chalcopyrite bioleaching

The rate of chalcopyrite bio-dissolution was tested against shrinking core models through diffusion control, chemical control, and mixed control. Kinetic data showed a good fit (Figure 4) to the diffusion controlled model according to Eq. [5]

$$1- 2/3x - (1-x)^{2/3} = k_d.t \tag{5}$$

The dissolution of copper proceeded by the diffusion of Fe(III) as the lixiviant generated bio-genically, through the porous product layer viz. jarosite formed on the ore particles, as indicated by XRD analysis also. The rate-constant values for the diffusion controlled bio-leaching of copper with unadapted isolate were obtained from Figure 4A as 0.007, 0.013 and 0.025d^{-1} at 25°C (298K), 30°C(303K) and 35°C (308K) respectively. The range was quite similar with adapted isolates as well (Figure 4B). The kinetic data for various particle sizes also fitted well to the diffusion control model. The plots of rate-constant values (k_d) with the reciprocal of r^2 (r being the size of the particles used) at 35°C for un-adapted and the adapted bacteria, showed straight lines (not given here) which further confirmed that the copper bio-leaching followed the diffusion controlled model (Gbor and Jia, 2004). The activation energy values (E_a) were calculated from the Arrhenius plots (Figure 5) and were found to be 9.6 and 10.8 kJ/mol respectively for the leaching with the un-adapted (Bevilaqua et al., 2002, Qiu et al., 2005; Zhang et al., 2008) and adapted isolates (Xia et al., 2008) under the temperature range 298-308K at 2.0pH.

The XRD phase analysis of the residue obtained during bio-leaching at 35°C with the adapted culture showed that hydronium jarosite [$H_3OFe_3(SO_4)_2(OH)_6$] and quartz were present as major phases (Xia et al., 2008) and chalcopyrite and pyrite as the minor phases.

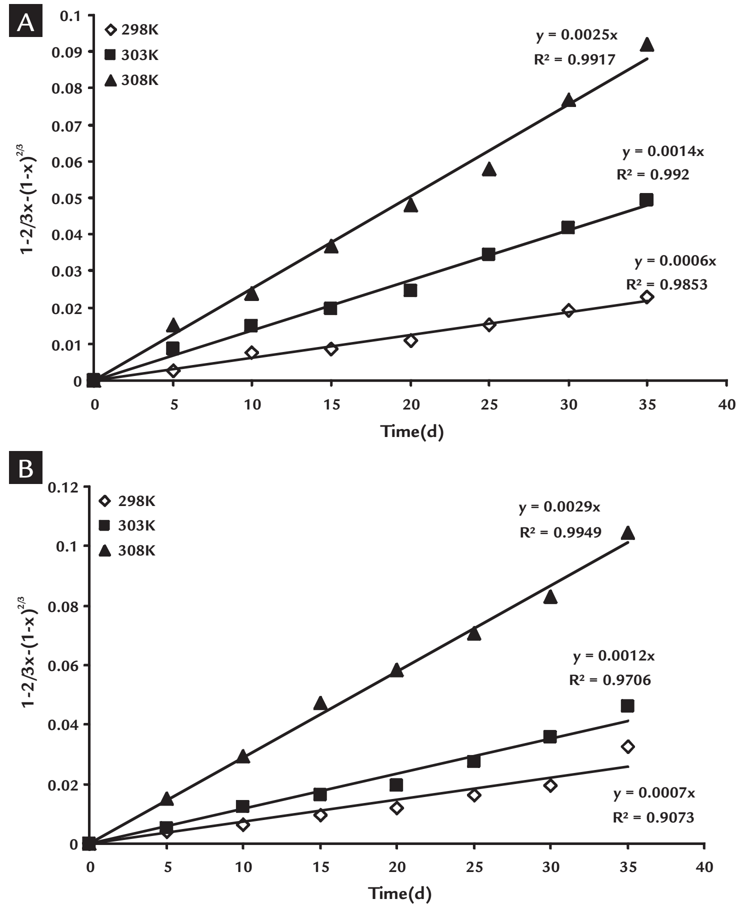

Figure 4
Diffusion Control model for bioleaching of chalcopyrite (A-with un-adapted bacterial culture, B-with adapted bacterial culture on ore).

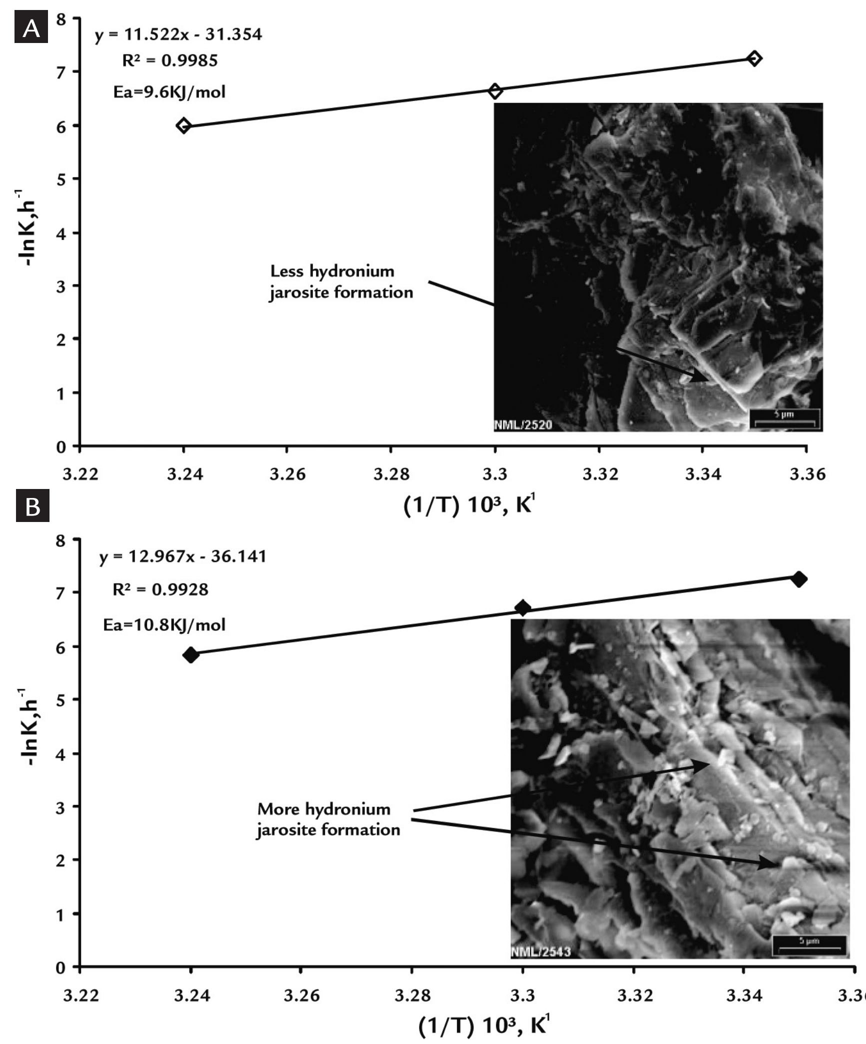

Figure 5
Arrhenius plot for bioleaching of chalcopyrite by bacteria culture (A-with un-adapted cells, B-with adapted cells).

4. Conclusions

1. The native culture of mesophilic bacteria predominantly *A.ferrooxidans* isolated from the source mine water show good potential for the bio-leaching of copper from the low grade ore.
2. A bio-recovery of 75% copper in leach liquor is achieved with the ore adapted culture at 2.0pH with the particles of < 50µm size in 35days time.
3. The bio-dissolution of copper follows diffusion controlled kinetic model with the reaction of bio-genically produced Fe(III) through the porous product layer comprising of jarosite formed during the process.
4. The copper bio-dissolution is facilitated by the presence of Fe(III) ions and higher redox potential generated during the course of leaching.
5. The activation energy acquired in the bio-leaching is found to be 9.6 and 10.8 kJ/mol for the un-adapted and the ore adapted culture respectively in the temperature range 25-35°C.

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