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TECHNICAL ARTICLE

Treatment of Lignite Mine Water with Lignite Fly Ash and Its Zeolite

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Abstract

As expected, a zeolite formed from lignite fly ash proved to be far more effective in treating the water from the Neyvelli lignite mines than the fly ash itself. Treatment of mine water at different doses with both materials revealed that the zeolite increased the pH from 2.73 to 8.58 and removed most of the hardness, including the Ca and Mg hardness, as well as the acidity from the mine water. In contrast, the fly ash increased the hardness, Ca, Mg, and sulphate in the mine water. The fly ash was partially effective in removing metals like Mn, Ni, Zn, and Cr. In contrast, increased dosing of lignite fly ash zeolite removed 98.6% of the Mn, 99.94% of the Fe, 96.35% of the Ni, 99.30% of the Cu, 19.15% of the Cd, and 100% of the Zn, Pb, and Cr from lignite mine water. The surface of the lignite fly ash particles were initially covered with loosely attached metals that were released in the acidic water, though due to its alkaline nature, it did partially remove the metals from the mine water.

Keywords Fly ash zeolite · Acid mine water · Batch experiment · Cation exchange capacity

Introduction

The Neyvelli Lignite Corporation Ltd (NLC) is a government-owned lignite mining and power generating company in India. NLC operates the largest open pit lignite mines in India, is presently mining 24 MT of lignite, and has an installed capacity of 2740 MW of electricity. The generation of acid mine drainage (AMD) represents a major environmental issue associated with the lignite mining industry. In Neyvelli, NLC is making efforts to minimize treatment costs (Maree and du Plessis 1994; Maree et al. 1998; Labuschagne et al. 2005). Other agents like blast furnace slag, lignite fly ash, and synthetic zeolites have been investigated as an alternative to conventional lime neutralization (Xenidis et al. 2002; Doye and Duchesne 2003; Feng et al. 2004; Rios et al. 2008). Fly ash zeolite (FAZ) has also been successfully used to treat AMD (Moreno et al. 2001; Cama et al. 2005; Somerset et al. 2008; Prasad and Mortimer 2011; Prasad et al. 2013).

FAZ was first prepared by Holler and Wrishing (1985), followed by many workers who synthesized FAZ from fly ash by hydrothermal activation (Derkowski et al. 2007; Murayama et al. 2008; Prasad et al. 2012; Sommerville et al. 2013). Zeolite mineralogy and cation exchange properties depends on the composition of the fly ash, concentration of reacting alkali, time, pressure, temperature, and the solid: liquid ratio (Mondragon et al. 1990; Quirol et al. 2002; Inada et al. 2005; Moriyama et al. 2005). The use of lignite FAZ as a low cost material to treat lignite AMD has rarely been investigated (Grigorios et al. 2015). So, the main objective of the present study was to convert lignite fly ash into zeolite and use it for lignite mine water treatment. The Neyvelli lignite mine and its power plant are located within 10 km of each other, which will reduce transportation costs and enhance the economics of its use.

Methodology

Acid mine water was collected from Mine-1 (B4) and Mine-1A (AS6), which are the active NLC mine sites. The AMD was collected in two 25 l plastic containers, which were initially rinsed with AMD before sampling. The pH and conductivity were analysed immediately at the field site in each sample using a Eutech Instrument multi-parameter tester (35 series) and were found to be similar. Samples were then immediately brought to the laboratory and kept refrigerated until used. Fresh lignite fly ash was collected from the electrostatic precipitator of the Neyvelli lignite thermal power

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plant. The ash samples were bench dried at room temperature and calcined at 800 °C to remove unburnt carbon and volatile materials. Synthesis of zeolite was carried out based on previous work (Prasad et al. 2012, 2013). The chemical composition of the fly ash and its zeolite was determined by X-ray fluorescence (XRF) using a Philiphs PW 2400 XRF spectrometer. Sample mineralogy was determined by powder X-ray diffraction (XRD) analysis using a model Rigaku ultima IV. Photomicrographs of fly ash and FAZ before and after treatment was obtained using a Jeol JSM 6510 scanning electron microscope (SEM).

The treatment of lignite mine water with different doses of lignite fly ash and its prepared zeolite was carried out at laboratory scale. Batch experiments were carried out at room temperature, with continuous stirring in a 250 ml conical flask, using aliquots of 225 ml of each water sample and lignite fly ash/zeolite powder doses from 5.0 to 60 g l^{-1}. Three replicas were performed for each experiment and the final result was the calculated mean of the three values. The mixtures were filtered after an hour of stirring using Whatman 42 filter paper of 2.5 µm pore size. The concentrations of total hardness, Ca, and chloride were analysed using titration technique (Arnold et al. 1992). Magnesium hardness was calculated as the difference between total hardness and Ca hardness. Acidity was determined by titration using NaOH solution and a phenolphthalein indicator. Sulphate was determined by a gravimetric technique, using barium chloride solution and precipitating the sulphate as barium sulphate. A portion of the original mine water was filtered and acidified to a pH less than 2 and kept for analysis by atomic absorption spectrophotometer (AAS) using Thermo Fisher Model M Series Thermo Electron Corp., Cambridge, UK. All of the treated mine waters were filtered, digested, concentrated, and prepared for analysis by the same method (Arnold et al. 1992). The analysis of Cu, Mn, Pb, Fe, Cd, Zn, Ni and Cr was performed by calibrating the instrument with different dilutions of standard solutions, and performed at 324.7, 279.5, 217.0, 248.3, 228.8, 213.9, 232.0, and 357.9 nm, respectively. Distilled water acidified with nitric acid was used as a blank as well as a control. Three replicates were run for each sample and the instrument was recalibrated after every ten samples. The relative standard deviation was obtained for all samples. Because the treated samples were concentrated during digestion, the final results were calculated from the observed concentrations.

Results and Discussion

Characterisation of the Fly Ash and Fly Ash Zeolite

The lignite ash contains a high percentage of SiO_2 and Al_2O_3 (Table 1), which makes it suitable for zeolite synthesis (Tsishvili et al. 1992). The SiO_2 content decreased by about 6% during zeolite synthesis, while the SO_3 content decreased from 13.7 to 1.7%. The Na_2O content increased from 1.52 in the fly ash to 21.1% in the lignite FAZ, as the Na was incorporated in the FAZ structure. The Na_2O content of 17.05% in exhausted zeolite samples indicated that it still was able to remove contaminants from mine water. The increased LOI content reflects the fact that water molecules were incorporated in the zeolite structure.

XRD analysis of the lignite fly ash and its zeolite was conducted to determine the crystalline phases present. The crystalline phases in fly ash are quartz and mullite. The XRD results of the zeolite show that sodium aluminium silicate hydrate was formed. These aluminium silicate hydrates consist of zeolites like NaP1, fauzasite and chabasite (Cama et al. 2005; Prasad et al. 2012).

SEM photographs of the lignite fly ash and its zeolite indicates that the fly ash particles (Fig. 1) before treatment are spherical in nature and have a smooth surface due to a covering of alumino-silicate glass. The absence of spherical particles and the development of rough surfaces indicates that zeolite was formed on the surface of the fly ash particles by the hydrothermal treatment (Fig. 2).

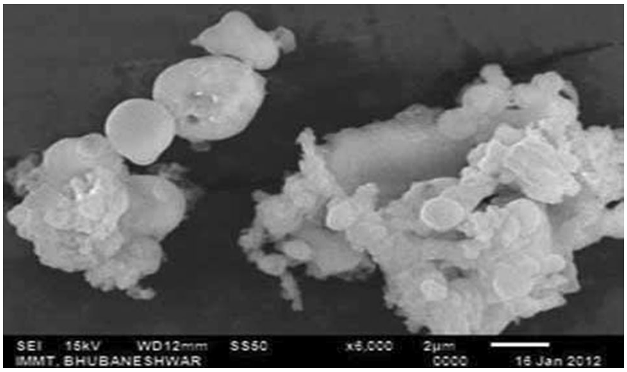

Fig. 1 SEM of lignite fly ash

Table 1 Chemical composition of lignite fly ash, fly ash zeolite and exhausted zeolite

Sample details	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	MnO	Na_2O	P_2O_5	SO_3	TiO_2	MgO	LOI	Conc. (%)
Lignite fly ash	37.281	28.265	2.906	9.11	0.127	0.014	1.515	0.062	13.76	1.53	3.485	1.78	99.835
Lignite FAZ	31.507	29.162	3.02	7.774	0.093	0.015	21.07	0.037	1.762	1.494	2.231	2.04	100.205
Ex. Lig. FAZ	31.469	29.526	3.992	8.232	0.107	0.017	17.05	0.044	2.341	1.475	2.514	2.36	99.127

Removal of Contaminants from Mine Water by Lignite Fly Ash and Zeolite

The collected untreated AMD was visibly transparent and had a pH of 2.73. It had high concentration of acidity, total hardness, sulphate, iron and various other metals (Tables 2, 3).

Results of total hardness, calcium, magnesium, chloride, sulphate, and acidity removal as a function of fly ash and FAZ dosage with mine water are given in Tables 2 and 3.

Increasing the dose of fly ash also increased the concentrations of total hardness, calcium, magnesium, and sulphate (Table 2). As lignite fly ash itself contains about 10% of CaO, instead of removing hardness from mine water, it contributed a marked increase in total hardness and calcium hardness concentration with increasing doses of lignite fly

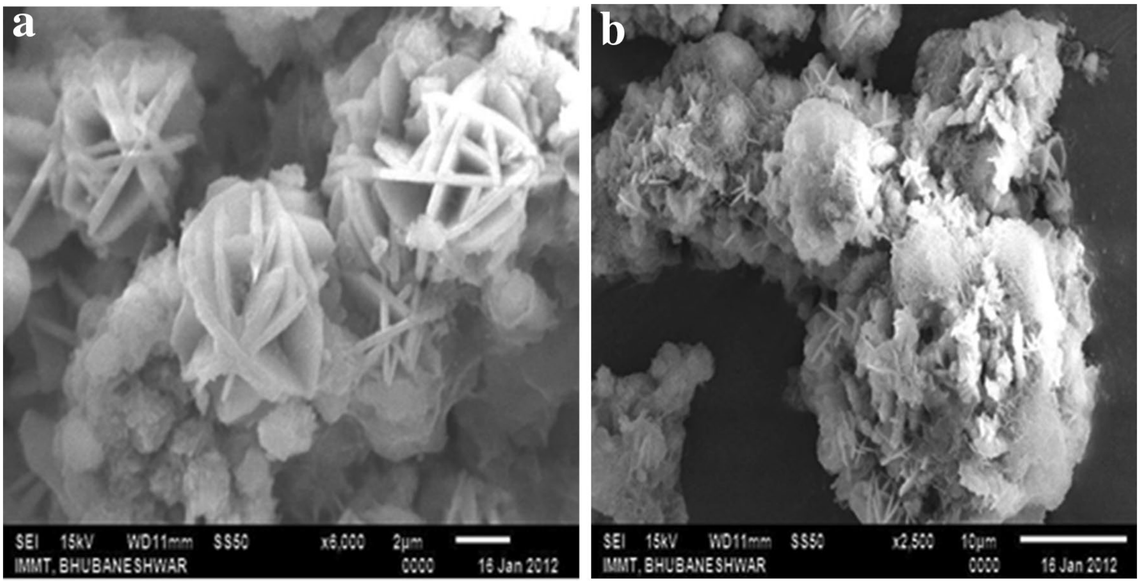

Fig. 2 SEM of lignite fly ash zeolite

Table 2 Reduction in concentration of different parameters in mine water (in mg/L) with different doses of lignite fly ash

Dose fly ash	Total hardness	Calcium as Ca	Magnesium as Mg	Chloride	Sulphate	Acidity	pH
Nil	280	152	31.10	120	743.39	674	2.73
5 g l^{-1}	620	430	46.17	120	855.72	328	4.43
10 g l^{-1}	755	595	38.88	120	1018.88	280	4.54
20 g l^{-1}	950	790	38.88	120	1187.38	196	4.65
30 g l^{-1}	1175	990	44.96	120	1350.54	136	4.77
40 g l^{-1}	1405	1210	47.39	120	1535.52	40	5.66

Table 3 Reduction in concentration of different parameters in mine water (in mg/L) with doses of lignite fly ash zeolite

Dose FAZ	Total hardness	Calcium as Ca	Magnesium as Mg	Chloride	Sulphate	Acidity	pH
Nil	280	152	31.104	120	743.39	674	2.73
5 g l^{-1}	424	296	31.104	120	709.46	112	4.80
10 g l^{-1}	396	248	39.964	120	767.56	32	6.43
20 g l^{-1}	232	148	20.412	120	744.28	20	7.55
30 g l^{-1}	148	92	13.608	120	731.71	14	7.92
40 g l^{-1}	128	72	13.608	120	746.13	8	8.05
60 g l^{-1}	76	40	8.748	120	762.61	Nil	8.58

Table 4 Concentration of elements in lignite acid mine water after treatment of lignite fly ash and lignite fly ash zeolite (in mg l^{-1})

Elements	Initial Conc.	Neyveli lignite fly ash					Neyveli lignite fly ash zeolite					
		5 g	10 g	20 g	30 g	40 g	5 g	10 g	20 g	30 g	40 g	60 g
Cu	0.319	0.201	0.149	0.064	0.021	0.012	0.063	0.013	0.011	0.010	0.008	0.002
Mn	0.196	0.176	0.158	0.163	0.160	0.134	0.146	0.091	0.028	0.009	0.003	0.000
Fe	64.857	1.404	1.437	1.480	1.398	0.835	0.565	0.324	0.051	0.026	0.037	0.038
Zn	1.266	1.174	1.138	1.049	0.974	0.739	0.785	0.238	0.00	0.00	0.00	0.00
Pb	0.010	0.002	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.790	0.750	0.677	0.655	0.637	0.569	0.657	0.460	0.170	0.075	0.065	0.029
Cd	0.005	0.007	0.008	0.008	0.008	0.007	0.004	0.004	0.004	0.003	0.003	0.002
Cr	0.140	0.031	0.036	0.023	0.026	0.008	0.004	0.00	0.00	0.00	0.00	0.00

ash. The lignite fly ash also contained more than 13% sulphate. Due to this, a marked increase in sulphate concentration was observed. Initially, the mine water contained 743 mg l^{-1} of sulphate but due to contact with 60 g l^{-1} dose of lignite fly ash, sulphate concentration increased to 1536 mg l^{-1} in the mine water. The alkaline lignite fly ash helped decrease the acidity in the mine water. Thus, lignite fly ash was not effective at removing ions from AMD, but instead released ions into the mine water. In contrast, with the increasing dose of FAZ, from 5 to 60 g l^{-1}, there was a considerable decrease in concentrations of total hardness, calcium, magnesium, and acidity (Table 3), with at least part of the decrease in acidity was due to the high alkalinity of the FAZ. Treatment of mine water with 20 g l^{-1} of FAZ produced the desired level of total hardness, 232 mg l^{-1}, since the allowable limit of total hardness in drinking water is 300 mg l^{-1}, as specified in Indian Standard: 10500.

Removal of Metals with Lignite Fly Ash

The pH of the Neyveli lignite mine water was 2.73 and the acidity was 674 mg l^{-1}. The initial concentration of different metals in lignite mine water is shown in Table 4 and Fig. 3a–h. Lignite mine water also contained higher concentrations of metals with a very high concentration of Fe (64.86 mg l^{-1}). Lignite fly ash was more efficient in removing metals (Fig. 3) from AMD than coal fly ash (Prasad and Mortimer 2011). This may be because it contains high percentage of CaO (almost 10%). When lignite mine water was treated with a dose of 5 g l^{-1}, the lignite fly ash had high removal efficiencies. For example, the Fe, Pb, and Cr removal efficiencies were 97.83, 74.73, and 78.14%, respectively. Moderate removal efficiencies for Cu, Mn, and Zn of 36.8, 10.45, and 7.3% were obtained, but Cd was not effectively retained. However, the Cd concentrations in the mine water was very low (0.004 mg l^{-1}) and it was not removed very efficiently by FAZ either (Fig. 3g).

Increasing the dose of the lignite fly ash further increased metal removal. One hundred percent of the Pb was removed at a dose of 10 g l^{-1} (Fig. 3) and 96.26% of the Cu, 98.71% of the Fe, 92.28% of the Cr, 31.46% of the Mn, 41.68% of the Zn, and 27.87% of the Ni were removed at a dose of 40 g l^{-1}. Only Cd was observed to increase at the higher fly ash dosage. Overall, the lignite fly ash was more effective than coal fly ash in AMD treatment (Prasad and Mortimer 2011), may be due to its higher alkalinity, pH, and CaO content, which would help precipitation and removal of more metals.

Removal of Metals with Lignite Fly Ash Zeolite

Lignite FAZ was more efficient than the fly ash in removing metals from lignite AMD (Table 4; Fig. 3a–h). A number of factors like the higher CEC, Na content, and alkalinity of the lignite FAZ was responsible for the high percentage removal of metals. At a dosage of 5 g l^{-1} FAZ, 100% of the Pb, 99.13% of the Fe, 97.29% of the Cr, and 80.31% of the Cu were removed, followed by 38.04% of the Zn, 25.80% of the Mn, 16.68% of the Ni, and 14.89% of the Cd (Fig. 3a–h). At increasing dosages, more metals were removed. Overall, even at low doses, the FAZ was highly effective at removing metals that have a high affinity for cation exchange (Prasad and Mortimer 2011). Almost complete removal of metals took place at higher FAZ dosages due to greater CEC and more sites for adsorption, thus counteracting competition between the cations for sites (Prasad and Mortimer 2011).

Conclusion

The pH of the mine water from the Neyveli lignite mines was approximately 2.73 with high concentrations of acidity and metals. The lignite fly ash can be easily converted into FAZ because it contains a high percentage of silica and alumina, which are required for zeolite synthesis. The lignite mine water was effectively treated with the lignite FAZ. The raw fly ash was not effective at removing hardness, calcium, magnesium, and sulphate from the mine water. Increasing the fly ash dose increased the concentrations of hardness, calcium, magnesium, and sulphate while an increasing FAZ

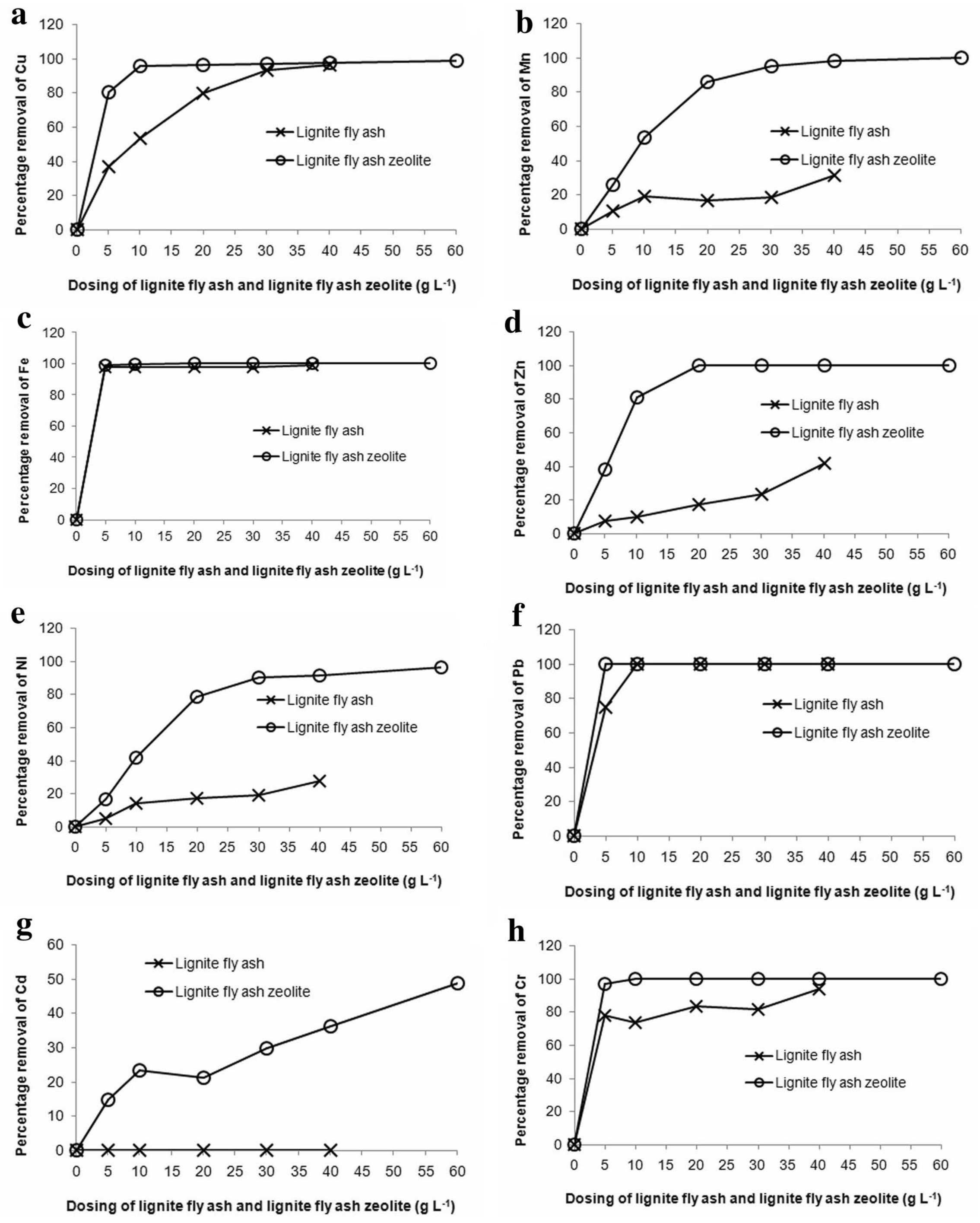

Fig. 3 Percentage removal of Cu (**a**), Mn (**b**), Fe (**c**), Zn (**d**), Ni (**e**), Pb (**f**), Cd (**g**), Cr (**h**) from lignite mine water after treatment with different doses of lignite fly ash and lignite fly ash zeolite

dose considerably decreased the concentrations of hardness, calcium, magnesium and acidity. Lignite fly ash and its zeolite were also evaluated for their ability to remove metals from lignite mine water. The results demonstrate that lignite fly ash efficiently removed some metals (Cu, Mn, Fe, Zn, Ni, Cr to some extent and 100% of the Pb) from the lignite AMD, though it was ineffective in removing Cd. Comparatively, the FAZ efficiently removed almost 100% of most of the metals from mine water. This FAZ can be effectively used to treat lignite mine water for it increased the pH, reduced hardness, acidity, metals, and many positively charged ions. Overall, we found that 20 g l^{-1} of FAZ was optimal in reducing the acidity, hardness, and metals, and it also increased the pH of the water to an acceptable level. Approximately 20 kg of FAZ would be needed to treat 1000 litre of AMD with a pH less than 3.0. Further consideration of regeneration and recycling of the exhausted zeolite would make the treatment process more economical.

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